DISPERSE SYSTEMS IN GASES;
DUST, SMOKE AND FOG

A GENERAL DISCUSSION

A GENERAL DISCUSSION ON DISPERSE SYSTEMS IN GASES; DUST, SMOKE AND FOG.

THE SIXTY-FOURTH GENERAL DISCUSSION OF THE FARADAY SOCIETY was held in the Department of Chemistry of the University of Leeds from the 20th to 22nd April, 1936, inclusive.

The subject was considered under two heads :—

Part I. : The General Properties and Behaviour of Disperse Systems, composed of :—

 (a) Solid and Liquid Non-Volatile Particles, *i.e.* Smoke, Dust, Oil Fogs, etc.

 (b) Aqueous and Other Volatile Particles, *i.e.* Mist, Cloud, Hygroscopic Nuclei, Town and Country Fogs.

Part II. : The Industrial Aspects of Disperse Systems in Air and Gases.

In the absence of the President, the Chair was occupied in succession by Sir Robert Robertson and Professor F. G. Donnan, Past Presidents.

By the courtesy of the Vice-Chancellor and the Refectory Committee, the Guest Night Dinner was held on Tuesday, 21st April, in the Refectory.

At the Inaugural Meeting, the Vice-Chancellor of the University, Sir James Baillie, welcomed the Society to Leeds, and Sir Robert Robertson then introduced the overseas guests, visitors and members, who were received with acclamation. The following were so welcomed : Professor J. Firket (Liege), Dr. E. Hiedemann (*Köln*), Professor H. Köhler (*Uppsala*), Dr. and Frau R. Meldau (*Berlin-Charlottenburg*), Dr. J. L. van der Minne (*Amsterdam*), Dr. J. J. Nolan (*Dublin*), Dr. E. Proskauer (*Leipzig*), Professor H. Remy (*Hamburg*), Dr. P. Schuftan (*München*), Dr. H. Schmeel (*Darmstadt*), and Dr. P. Siedler (*Frankfurt a.M.*).

At the conclusion of the meeting, the thanks of those present were accorded to the overseas guests, to the Vice-Chancellor and Senate of the University, to Professor Whytlaw-Gray, Mr. Cawood, and other members of the organising committee, to the Refectory Committee, and to the contributors of papers.

The Report of the meeting, including all the papers contributed, together with the discussion thereon, appears in the following pages.

DISPERSE SYSTEMS IN GASES.

(General Introductory Paper.)

By R. Whytlaw-Gray.

Received 14th April, 1936.

The subject of this discussion includes a great variety of natural and artificial systems which are described by such terms as dust, smoke, fog, fume, haze, mist and cloud. All these consist of solid or liquid material dispersed to a greater or lesser extent in gaseous media. They all show a great tendency to change and none are permanent when compared with the more familiar colloidal solutions. Thus dusts settle, smokes coagulate, and clouds dissipate by evaporation.

This characteristic instability is clearly a consequence of the physical properties of the gaseous medium, the low density and low viscosity of which offers little resistance to the movement of the particles or to molecular diffusion. Hence in these systems the particles sediment under gravity or centrifugal force, diffuse by brownian motion, and evaporate or dissolve at a much greater rate than they would were the medium liquid. It must be remembered, too, that the smaller particles suspended in gases possesses an enhanced mobility on account of the discontinuities in the medium. For example, the majority of smoke particles lie between the size limits 5×10^{-6} and 5×10^{-5} cm., radius, whilst the mean free path of the molecules in air at normal pressure is of the order of 10^{-5} cms.

For the purposes of this meeting it is convenient to consider separately the behaviour of systems of non-volatile and volatile particles. To the former category belong most dusts and smokes and some industrial fogs such as tar fogs, and to the latter the majority of natural systems such as country fogs, mist, etc., in which the particles are composed of water or of dilute aqueous solutions of hygroscopic nuclei. It is obvious that there is no clear dividing line between these two classes. Thus a sulphuric acid cloud in dry air would belong to the former and in moist air to the latter, again the particles of tobacco smoke rapidly absorb moisture and those in town air contain hygroscopic as well as carbonaceous material so that they readily condense water when the conditions are favourable. But it is evident that in many respects systems of non-volatile particles are simpler and certainly easier to investigate than those in which evaporation and condensation are additional and complicating factors.

Moreover these systems of non-volatile particles have in recent years attracted the attention of scientific workers both abroad and in this country so that a short summary of their properties may serve as a focussing point for this discussion.

Smoke.

Smoke is formed whenever the vapour of a substance of high boiling-point is diluted rapidly and cooled by admixture with a large volume

of air or any other gas.   This method applies to many systems.   Smokes can be formed also by chemical reactions at ordinary temperatures, indeed any reaction between gases or vapours resulting in the formation of a solid or liquid phase will when carried out in presence of a large excess of an indifferent gas produce a smoke.   Smokes then are formed from molecularly disperse material, by condensation, and in its early stages the process presents an analogy to the formation of a gold sol. There is however this important difference.   In the sol the gold origin-ally molecular, condenses around nuclei to form a stable two-phase system, the degree of dispersion of which is determined by the rate of formation of nuclei and by their rate of growth.   In a smoke although the process of formation is apparently analogous it results in the pro-duction of an unstable system and the primary particles formed by condensation on nuclei of the supersaturated vapour coagulate rapidly so that the degree of dispersion of the system changes continually with lapse of time.

Coagulation.

This property of continuous and spontaneous coagulation is the most striking characteristic of disperse systems in gases.   The smoke particles of whatever substance they are composed stick together when brownian motion brings them in contact.   Probably a high percentage of the collisions are effective and although this has not been proved by direct experiment, it has been shown that adherence results from the majority of collisions between smoke particles of different kinds with various surfaces.

By determining how the number of particles in a coagulating smoke diminish with time the course of the process can be followed quantita-tively.   Numerous smokes have been investigated in this way by different workers but the counting of smoke particles with the slit ultra-microscope presents unexpected difficulties and led originally to erroneous results.   Several methods are now available which agree among them-selves and the data obtained from these show that the coagulation of very many smokes follows a simple law.   If n_1 and n_2 represent the number of particles present per c.c. at times t_1 and t_2 minutes from the ormation of the system, then $1/n_2 - 1/n_1 = K(t_2 - t_1)$ where K is a constant.   Thus if the reciprocal of the number of particles present in a given volume of smoke are plotted against the corresponding times a straight line is obtained.

$1/n$ denotes the average space inhabited by a particle in the smoke at any instant of time.   It is termed conveniently the particulate volume and n the particulate number.   Although the validity of this relation-ship has been questioned there is so much experimental evidence to support it, that we believe it represents the course of coagulation of the majority of smokes to at least a rough approximation.

From this expression it is easy to see that the rate at which the particles disappear by coagulation depends only on the square of the number present and the constant K, i.e. $- dn/dt = Kn^2$.   In any given smoke, coagulation will be very fast in the early stages when the number concentration is high and later will fall off rapidly.   A comparison of the values of K obtained experimentally for different smokes in air under normal conditions of temperature and pressure shows no striking variation.   Clearly the coagulation process is to some extent independent

of the nature of the particles. The coagulation constant for any one smoke does, however, vary :—

(*a*) with the average size of the particle, fine smokes coagulate faster than coarse ones ;

(*b*) with the size distribution or range of sizes of the particles. When the size range is small the smoke approaches to the homogeneous, and systems of this type coagulate more slowly than ordinary smokes which are as a rule widely heterogeneous ;

(*c*) with the form and shape of the particles and the aggregates they form.

An ideal or perfect smoke would consist initially of even-sized spherical particles which on coagulation coalese to form progressively larger spheres. The kinetics of such a system were worked out for sols many years ago by Smoluchowski.

The theoretical treatment of smokes along those lines is more complicated because smoke particles lie between size limits which are comparable with the mean free path of the molecules of the gaseous medium. The simple mobility defined by Stokes' law has to be modified by terms, taking account of the discontinuous nature of the surrounding gas.

Smoluchowski's theory thus modified does, however, reproduce quite remarkably the experimental results obtained with smokes approximating to the above ideal conditions, as Patterson and Cawood have shown in their studies of stearic acid smokes.

It can be shown that the theory for a homogeneous smoke leads to an expression similar in form to that found experimentally : K, the so-called coagulation constant, being given by $K = \frac{4}{3}\frac{RT}{\eta N}\left(1 + A\frac{l}{r}\right)$, where $R =$ gas constant, $T =$ absolute temperature, $N =$ Avogadro's constant, $\eta =$ the viscosity of the medium, $l =$ mean free path of the gas molecules, r the radius of the particle, and A a constant.

Thus theory leads to the expectation that the particulate volume graph would be curved, K decreasing as coagulation proceeds. Actually the curvature is so slight for particles of the size found in homogeneous stearic acid smokes of the weight concentration used that it is doubtful whether it would be detected experimentally.

This expression also predicts the influence of pressure and temperature on the rate of coagulation as well as that of the size of particle and the viscosity of the medium. Up to the present the coagulation of smokes in gaseous media other than air has not been studied. Data, too, on the coagulation rate of small particles are scanty and the effects of temperature and pressure have hardly been investigated.

On the theoretical side the applicability of Smoluchowski's theory to ideal aerosols has been much discussed recently. Experimentally a really suitable smoke is difficult to obtain. Up to the present the nearest approximation to a perfect smoke would appear to be the homogeneous and reproducible stearic acid systems mentioned above, though a smoke such as that of paraffin in which the particles are liquid would possibly offer advantages.

Considerable progress has been made in the production of smokes for experimental purposes which approximate to homogeneity. It is clear from the nature of coagulation that a monodisperse system of primary particles can only be obtained by very rapid dilution of the molecularly disperse material.

This can be accomplished by volatilization in a rapid air blast, by chemical reaction at high dilution, or by photochemical decomposition as in the elegant method discovered by Winkel and Jander in which highly diluted iron carbonyl vapour is decomposed by light of short wave length. In all these methods even at the highest dilutions in which the weight concentration of the smoke is only of the order of a few milligrams per cubic metre, the number of particles a few minutes after the smoke is formed is several millions per c.c.

Extrapolation of the particulate volume graphs for this type of smoke shows that initially the number of primary particles must be very great.

A rough calculation from the dilution of a stearic acid smoke gives 10^{12} per c.c. and recently Fuchs and Oschman by diluting with great rapidity a sulphuric acid smoke have actually formed an aerosol consisting of primary particles. They found the number per c.c. 10^{11} and the size about 10^{-6} cms.

In these experimental smokes it is clear that the ultra-microscopic particles counted are aggregates of a large number of primary units and that the coagulation process is far advanced before counting is possible. The primary particles are amicroscopic. The possibility of obtaining stable systems of these is evident and opens up an interesting line of research. Atmospheric nuclei and large ions probably belong to this class. The rapid dilution of chimney smoke in a high wind may well form these systems and they are likely to be present in ordinary smokes in the early stages.

The rapidity of coagulation in systems of high number concentration is evident when the time taken to halve the number of particles is calculated. Using for this purpose the K value for a stearic acid smoke, *viz.:* $0·51 \times 10^{-9}$ cm.^{3} sec.$^{-1}$ we find for a system of 10^{11} particles per c.c. $t = 0·02$ sec., for 5×10^6 per c.c. $6·6$ minutes and for 10^5 per c.c. $5·5$ hours. To obtain a stable system of primary particles the original smoke must be diluted with 10^5 or 10^6 volumes of air in a fraction of a second.

So far practically nothing is known about the early stages in the formation of smokes. Probably as in sols, the rate of nuclear formation and velocity of their growth are important stages. Now that it is realised that smokes originate from highly dispersed amicroscopic primaries there is hope that methods of attacking these difficult problems will be developed.

It will be obvious from the foregoing considerations that the experimental smokes so far discussed are special types. Although the particles composing them are aggregates and formed from a large number of primaries they are at least approximately homogeneous. This is evident from their appearance in the field of the ultra-microscope. Unfortunately no satisfactory quantitative studies have been made of the size distribution of particles in smokes. Both from the point of view of the theory of coagulation and also from that of the actual composition of smoke much is to be learnt from such investigations.

The ordinary smoke of factory and domestic chimneys and, indeed, the great majority of industrial and laboratory smokes belong to the hecterogeneous type and exhibit a wide range in particle size forming frequently large loosely built aggregates of microscopic dimensions or irregular chains composed of small units. This structure which is characteristic of the particles in concentrated systems especially in

metallic oxide smokes must affect the mobility of the particles and their collision frequencies. Further, as Kohlschütter was the first to show the densities of such particles are very much smaller than that of the material composing them. Whether this structure revealed by the microscope is a replica on a larger scale of the structure of ultra-microscopic particles is an open question. The application of X-ray or electron diffraction methods to the examination of smoke films might here prove of considerable value and interest.

Up to the present no normal aerial systems have been discovered in which coagulation does not take place, and no counterpart to the sol stabilised by protective agents has been observed. Although the suspended particles in gases doubtless adsorb molecules of the medium, this effect appears to have little influence on their adhesion. It is possible that a stabilising action might be detectable in gases which are highly adsorbed by the disperse material. Again whether the particles carry electric charges or are electrically neutral has little affect on the rate of coagulation. It is well known that smoke particles readily catch ions of both signs from the surrounding medium and when formed in a highly ionised atmosphere, such as in the presence of X-rays or by high temperature reactions, are strongly charged, but the smokes contain as a rule equal numbers of $+$ and $-$ units and are usually electrically neutral. Highly charged unipolar smokes can, however, be formed and these might be expected to show a diminished rate of coagulation. This has been found by Fuchs to be the case for highly charged unipolar oil smoke, though experimental investigation is difficult on account of the space charge which quickly drives the particles to the walls of the containing vessel. In this investigation it is interesting to note that the splitting up of the complexes into simpler units was claimed to take place during charging.

The rate at which ions are caught by particles of various sizes and the limiting charge acquired in an ionic atmosphere of given intensity are important factors in electrical precipitation and will be discussed in communications to this meeting.

Apart from electrical precipitation which at the moment is probably the most practical way of removing fine particulate matter, a study of disperse systems in gases indicates the possibility of the development of other methods which may in the future have many applications. Theory indicates that the rate of coagulation is determined by the probability of encounter of particles in brownian motion. Any factor then, which will increase the sphere of influence or the mean free path of these smoke particles will hasten coagulation. The production of turbulence in the medium by the formation of eddies and vortices will bring this about to some extent though for fine particles it is not so effective as for larger.

Of great interest is the effect of sonic and supersonic waves in bringing about rapid coagulation. This has been studied both experimentally and theoretically in recent years, notably by Brandt and Hiedemann in Germany, and Andrade in this country, and striking results have been obtained.

The movements of smoke particles in a temperature gradient and the formation of a dust-free space around hot bodies has been known ever since the pioneering work of Aitken and of Lodge in the last century. Precipitation of smoke and dust on cold surfaces is a common phenomenon but the mechanism of the process and the forces involved has

never been satisfactorily explained.   Attention has recently been turned to a more detailed study of this effect and it has been utilised on a small experimental scale in the thermal precipitator for determining dust and smoke in disperse systems in gases.

Dusts.

Whilst smokes are formed by condensation, dusts whether natural or artificial are produced invariably by disintegration or dispersion processes.   Speaking generally they consist of larger particles which from their mode of origin are denser and composed of much larger units.   Hence they sediment more rapidly than smokes.   Again the number concentration in dust systems is usually low though on account of the size of the particles they reflect light and show a high optical density.   Dusts do, however, coagulate and the large primary units stick together when they come in contact forming complexes, but the process is slow and plays only a secondary part in their life history. Theoretically the coagulation of these systems presents interesting features but it has not so far been studied in any detail.   Another characteristic of dusts is the ease with which the particles acquire electric charges, probably produced by frictional effects.   In combustible materials such as coal dust this easily leads to dust explosions when the medium is air.

The toxic effects of siliceous dusts in industry are well known, but although much careful work has been done in this field, information on what size ranges of particles are the most harmful is still scanty. Progress in the investigation of dusts, and indeed of all disperse systems in gases, is largely a question of technique.   Until recently many methods used were open to criticism, but it is possible now to determine with accuracy the mass concentration, number concentration and size distribution in dusts.   The investigations of Green have done much to advance this aspect of the subject.

In this brief survey emphasis has been laid on spontaneous coagulation as a specific characteristic of these systems.   It must, however, be pointed out that the very dilute smoke which pollutes the air of cities, as well as the many natural systems included in the terms fog, mist, and haze, change only with extreme slowness on account of the low number concentration of their particles.   Nevertheless, coagulation even in these systems may be of significance, especially in the case of atmospheric nuclei and very small particles.

PART 1 (a). THE GENERAL PROPERTIES OF DISPERSE SYSTEMS COMPOSED OF SOLID AND LIQUID NON-VOLATILE PARTICLES (i.e. SMOKE, DUST, OIL, FOGS, ETC.).

ON THE PROPERTIES OF AEROCOLLOID SYSTEMS, WITH REGARD TO THEIR DEPENDENCE ON THE METHODS OF FORMATION.

By Karl Ernst Stumpf and Gerhart Jander.

Previous investigations have shown that in contrast with liquid sols, aerosols are invariably unstable systems which aggregate and sediment more or less rapidly. Hence the unstable condition of aerosols is only to be compared with the special case of the rapid coagulation of liquid sols.

In the investigation of aerosols, therefore, two important questions arise : (1) what properties do they possess in parallel with liquid sols, and (2) on what factors do the properties of aerocolloid systems depend. This paper will examine principally the problems associated with the second question.

The properties of liquid sols are determined mainly by (1) the nature of the dispersed material, (2) that of the dispersion medium, (3) the effect on the prepared sol of additions which influence the electrical charge of the disperse phase or exercise a protective colloid action, and (4) the method of preparation itself. We shall examine the extent to which the properties of aerocolloid systems are determined by these factors.

The aerosols hitherto investigated show real differences according to the chemical composition of the substance used. Thus mercuric iodide smokes and aerosols of certain dye stuffs [1] age specially rapidly, since the decrease in the number of particles and the increase in their size depend not merely on aggregation, but also on the isothermal distillation or sublimation taking place in these systems. These substances have an appreciable vapour pressure, which increases with increasing curvature of the surface,[2] *i.e.* with decreasing particle size, so that small particles evaporate more readily than large and the vapour condensing on the larger particles, still further increases their size.

However, in systems where isothermal distillation is absent, because of a vanishingly small vapour pressure, singularly rapid ageing has been observed, as in certain metallic oxide smokes,[3] *e.g.* ferric oxide smoke.[4] Whytlaw-Gray has shown that these systems aggregate in a special way with formation of chain-like aggregates. The individual particles possess to some extent a dipole nature ; they unite preferentially at the surfaces of the individual particle, at which it would grow preferentially as a crystal.

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[1] Whytlaw-Gray and Patterson, *Smoke,* London, 1932, 168 ff.
[2] W. Thomson, *Phil. Mag.* (4), 1871, **42**, 448.
[3] Whytlaw-Gray, *loc. cit.,* 51, 81 ff.
[4] Jander and Winkel, *Kolloid-Z.,* 1933, **63**, 5.

The formation of chain-like aggregates in aerosols also can depend on pyroelectric properties of the disperse phase. According to Beischer,[5] the needle-like crystals of aminoazobenzene, produced by cooling the supersaturated vapour, are charged pyroelectrically in such a way that each end carries an opposite charge. Hence it is understandable that the smoke would aggregate rapidly, forming chains such as Beischer has observed ultramicroscopically. Moreover, even in the absence of iso-thermal distillation or any special kind of aggregation, the differences arising from the physical properties of the various substances used as aerosols also leads to more or less rapid ageing. The rapid coagulation of unidisperse sols may be described by Smoluchowski's equation in the form,

$$\mathrm{d}n \qquad \tfrac{2}{3} \cdot \frac{RT}{=} \cdot n^2$$

where $-\dfrac{\mathrm{d}n}{\mathrm{d}t}$ is the velocity of disappearance of n particles present at time t. R is the gas constant, T the absolute temperature, η the viscosity of the dispersion medium, and N the Avogadro number. In this simplified form, the equation holds good provided that the effective radius of the particle is equal to its real radius, *i.e.* provided that the particles remain attached to one another only at an actual collision. This law, which has been applied by Whytlaw-Gray[6] to aerosols, presupposes spherical particles. This condition is fulfilled only in fogs or in smokes produced by cooling fogs if the solidifying droplet does not change its shape by crystallisation. The stearic acid smoke used by Whytlaw-Gray approximates to this ideal case. All smokes of substances difficult to melt or of readily crystallisable substances vary more or less widely from the above requirements, so that their more or less rapid ageing is understandable.

The properties of aerosols are, therefore, to a great extent dependent on the substance used.

So far as we know, no investigations have been made of the effect of the gaseous dispersion medium on the resulting colloid system. From Smoluchowski's equation, we should expect the viscosity of the medium to affect the coagulation velocity, in the sense that the velocity increases with decreasing viscosity.

Attempts to influence the behaviour of the prepared aerosol by electri-fication, or by the addition of " protective " substances, clearly show the great difference between liquid sols and aerocolloid systems. This is due to the difference in the dispersion medium, liquid or gas. Both in lyophobic and in lyophilic sols, the dispersion medium plays an important part in stabilising the sol, by making unipolar electrification possible or by ad-sorption at the surface of the particle. Whytlaw-Gray and his co-workers[7] and others[8] have nowhere indicated any such stabilising action of the dispersion medium on aerosols. At the slight degree of electrification, bipolar or unipolar, which certain methods of preparation produce, no measureable effect on the rate of ageing has been detected. Moreover, with the usual strong unipolar electrification, no stabilisation results. There must be other effects, unknown in liquid sols, which permit the disappearance of aerosols. N. Fuchs has shown recently[9] that strongly

[5] *Z. physik. Chem. A.*, 1936, **176**, 1.
[6] *Loc. cit.*, 57 ff.   [7] *Loc. cit.*, 146 ff.
[8] G. Jander and A. Winkel,[4] 10 ff.
[9] N. Fuchs and J. Petrjanow, *Acta Physicoch. U.R.S.S.*, 1935, **3**, 827.

charged unipolar aerosols do not aggregate, as might be expected, owing to the electrical repulsion between the particles; however, the cloud has a tendency to expand. The particles migrate to the walls of the vessel, to which they give up their charges and remain attached. Stabilisation would be obtained by unipolar electrification only if the walls of the vessel were charged, and of the same sign as the charges on the particles, so that the tendency of the particles to migrate to the walls would be compensated by the repulsion exerted on them by the correspondingly charged walls.

By analogy with liquid sols, stabilisation of aerosols by the action of protective colloids is conceivable, so long as these protective aerosols are stable as pure aerosols, *i.e.* so long as they do not aggregate on undergoing the collisions due to their Brownian motion, but collide elastically. Such aerosols are at present unknown; the majority of collisions between particles lead to aggregation. Aggregation may, however, be retarded by the addition of substances which are adsorbed at the surface of the particles,[10] an effect certainly not due to elastic collisions between the protected particles. Probably the effect is to be ascribed to impedance of factors which accelerate ageing, such as isothermal distillation, or the formation of polar crystalline particles. The stabilising substances so far used (*e.g.* phenol or oleic acid) cannot be added subsequent to formation of the aerosol, but must be evaporated along with the substance forming the sol, so that they condense with it. No experiments (particularly with regard to a possibly expected retardation of the coagulation velocity) have been made with subsequent additions of vapour to be adsorbed as a protective envelope.[11] So far, then, attempts to stabilise aerosols, either by electrification subsequent to preparation, or by the addition of other substances, have achieved no real success.

In contrast with liquid sols, therefore, the properties of a given aerocolloid system are fixed as soon as its preparation is complete. Of the more important methods of preparation, the first comprises the subdivision of a coarser system * to one of particles of colloidal dimensions. The second method involves producing a colloidally disperse phase by aggregation or coagulation from a molecularly disperse (gaseous) phase. All the usual methods of preparation depend on this condensation process methods. It may be further subdivided into three groups, the physical, chemical and photochemical condensation methods.[12]

In the physical condensation method, the substance to be investigated is heated to produce evaporation of a considerable mass and the disperse colloid phase results by subsequent condensation. In this way, aerosols of a large number of inorganic and organic substances have been prepared.

By chemical condensation methods, two substances in the form of vapour react with the formation of a product, whose vapour pressure at ordinary temperatures is very slight, or practically zero (*e.g.* NH_4Cl smoke from HCl and NH_3; H_2SO_4 fog from SO_3 and steam and metallic oxide smokes from zinc ethyl or from base metals evaporated in the arc with atmospheric oxygen).

By the photochemical condensation method, a substance suitably illuminated yields an aerosol product of vanishingly low vapour pressure. So far, only ferric oxide dusts, resulting from the photochemical decomposition of iron pentacarbonyl, have been obtained by this method.[4]

In order to obtain reasonably reproducible results, it was necessary to improve the methods of preparation of aerosols. Using a physical conden-

[10] A. Winkel and G. Jander, *Schwebstoffe in Gasen*, Stuttgart, 1934, 43.
[11] H. Remy, *Z. angew. Chem.*, 1933, 46, 610, and earlier papers; A. Krassil-chikov, *Kolloid Z.*, 1936, 74, 138.
* The atomisation of liquids is the outstanding example, and is unimportant since only relatively coarse, rapidly aggregating polydisperse systems are obtained. It is excluded, therefore, from consideration.
[12] V. N. Fuchs, *Über die Bildung von Aerosolen; Acta Physicoch., U.R.S.S.,* 1935, 3, 61.

sation method, Whytlaw-Gray [13] succeeded in preparing highly reproducible aerosols, especially of stearic acid, by using a constant weight of the fog-forming substance and carefully maintaining every detail in the preparation unchanged, otherwise aerosols of different behaviour resulted. The substance was heated in a stream of air in an electrically-heated boat, and the vapour-charged air stream was rapidly cooled by dilution with the cold air in the chamber. If the substance was evaporated directly into the chamber and distributed by stirring, the resulting aerosols at once coagulated more rapidly to much coarser systems, a method which is less exact and yields only poorly reproducible aerosols.

With chemical condensation methods also, finely divided, reproducible aerosols cannot be obtained if the gaseous reactants are mixed directly in the chamber. Fuchs and Oschman [14] have, however, prepared very finely divided and highly reproducible fogs from sulphur trioxide and air containing water vapour, by greatly diluting the reactants and allowing them to react after thorough mixing (by the method they describe) before introduction and distribution through the chamber ; the system is rapidly diluted to the concentration at which the investigation is carried out, perhaps simultaneously with the completion of condensation and the beginning of coagulation. This method is only suitable, however, for the production of finely divided and very dilute fogs. Whytlaw-Gray has shown that the electric arc as a means of preparing smokes under reproducible conditions is still less suitable.[15] In contrast to those prepared by other methods, aerosols prepared by the arc are mainly charged and of both signs and, moreover, the formation of chain-like aggregates is clearly shown, a property due more to the nature of the metallic oxide than to the method of preparation.

The ferric oxide dusts [4] prepared by the photochemical condensation method are exceptionally finely divided and highly stable sols with extreme reproducibility.

The most finely divided and most stable systems (and the most reproducible) result by using methods in which the condensation proceeds under the most uniform conditions, and the freshly formed very finely divided aerosol can be equally rapidly and uniformly distributed through the chamber ; they age more slowly than aerosols prepared in other ways. According to Müller's theoretical treatment of hydrosols,[16] polydisperse systems coagulate more rapidly than unidisperse systems of the same concentration and particulate number. Approximation to complete unidispersity can only be realised in the very earliest stages, since with the onset of aggregation the condition of uniformity is immediately destroyed. For all quantitative investigations, therefore, it is simpler to use systems which are as unidisperse as possible.

To obtain reproducible, unidisperse systems, special attention must be paid to the conditions under which condensation and coagulation up to the time of uniform distribution in the chamber take place. Our knowledge of the course of these two important processes is slight. Scarcely any work has been carried out apart from investigations on water fogs,[17] on the rôle played in condensation by condensation centres and foreign nuclei. According to Whytlaw-Gray's views,[18] for substances of very low vapour pressure, like stearic acid and arsenic, so high a degree of supersaturation will be produced that the molecules of the vapour itself become effective centres for condensation, so that no foreign nuclei need to be assumed. This will only be the case, however, if the cooling and consequent

[13] *Loc. cit.*, 44.
[14] *Acta Physicoch.*, *U.R.S.S.*, 1935, **3**, 65.
[15] *Loc. cit.*, 76, 77.
[16] Wiegner and Tuorila, *Koll-Zeitschr.*, 1926, **38**, 3.
[17] See Freundlich, *Kapillarchemie*, 4 Aufl., 1932, 2 Bd. 780 ff.
[18] *Loc. cit.*, 74 ff.

high supersaturation are accomplished rapidly. Now, the cooling of the vapour takes time, and proceeds through all stages from saturated vapour to a state of high supersaturation. At the beginning of condensation, the larger foreign nuclei will act as centres at which larger aerosol particles will be formed. In time, greater supersaturation will ensue, and in addition to the larger particles already present, smaller particles will be formed with the molecules of the substance itself acting as condensation centres. Thus the kind of cooling (*Abschreckung*) will exercise a profound influence on the nature of the aerosol. The faster the cooling, the faster will the critical region (in which larger particles are formed at foreign nuclei) be passed through, leading to a correspondingly more finely divided and uniform aerosol. In the chemical and photochemical condensation methods, the " chilling " is instantaneous, and hence the magnitude of the supersaturation depends on the speed of the reaction.

Moreover, even in respect of the coagulation which occurs prior to distribution in the chamber, rapid cooling of the condensing vapour is valuable. From Smoluchowski's equation describing the course of coagulation given above we may deduce the effect of temperature, viscosity of the medium and particle concentration on the rate of coagulation. The higher the temperature and the higher the particle concentration, the more rapidly will the aerosol age. If, therefore, cooling is effected slowly, aggregation to coarser particles will proceed proportionately rapidly. The original concentration of the vapour to be condensed similarly influences the aerosol produced ; the higher the vapour concentration, the higher the concentration of the resulting aerosol, and the more rapidly will it aggregate. This explains why direct evaporation in the chamber and distribution of the vapour by mere stirring results in coarse heterogeneous systems. In this case, the density of vapour is high at the start, the cooling is in no way uniform and relatively very slow, whereas, if the substance is heated in a tube and blown into the chamber, the vapour and the aerosol concentrations are low, so that by the more rapid and more uniform cooling, a more unidisperse system is distributed through the chamber by the stirring apparatus. Reproducible results can, therefore, be obtained by accurate control of the temperature of heating, velocity of the air stream and rate of stirring in the chamber. Reproducibility is also related to the amount of substance dispersed as fog, in that at the same temperature, a correspondingly longer time is required for the evaporation of a larger amount of material. As a result, whilst the last portions of the substance are evaporated, the earlier portions are already distributed throughout the chamber as aerosol to which the small primary particles rapidly unite with particles which are already aggregated. This explains why arsenic dusts prepared under the same conditions showed different behaviour according to the concentration.[19]

Fig. 1, taken from the paper cited, shows that the more concentrated systems are actually more polydisperse than the more dilute systems. Owing to the longer time needed for the preparation, the final portion evaporated, condenses and aggregates on the particles first formed. By the rapid sedimentation of the large particles thus formed, the average weight of the particle at first quickly falls, until a finely divided and homogeneous system remains ; it then begins to rise as expected, owing to coagulation. Since the more dilute systems, owing to their shorter time of preparation, are already uniform, the change of particle weight with time is as expected from the start.

In addition to the condensation and initial coagulation at greater concentrations, the method of distribution in the chamber is of importance in securing uniformity in the resulting system, otherwise imperfect results are obtained. Even when the formation of the aerosol is practically complete before its entry into the chamber, uniform distribution, to which

[19] G. Jander and A. Winkel, *Kolloid-Z.*, 1933, **65**, 290.

stirring contributes, opposes homogeneity in the particle size, despite the most careful experimental conditions. This can be roughly confirmed by first distributing the vapour uniformly in the experimental vessel and then effecting sudden condensation, either by cooling or by adiabatic expansion. Condensation invariably occurs partly in the concentrated vapour and partly only during the final distribution in the chamber. Thus, aggregation occurs at different concentrations until uniform distribution has been secured, so that it is never possible to achieve more than approximate homogeneity and reproducibility.

The same state of affairs arises with the chemical condensation methods. If the reactants are first mixed in the chamber, a heterogeneous, rapidly coagulating aerosol results. It is only when the reaction is practically completed before the mixture enters the chamber under constant conditions that highly reproducible fogs are obtained, as Fuchs [14] has shown.

The degree of uniformity secured by the methods so far used depends on the extent to which it is possible to direct and influence reproducibly, the condensation process and the coagulation occurring in the short time prior to entry into the chamber. This cannot be done rigourously, since
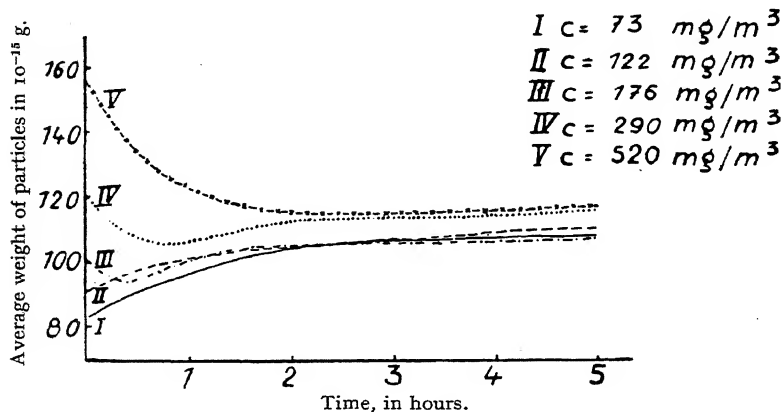

FIG. 1.

the two processes follow one another with differences of time and place. The systems thus result from a complex procedure, and must themselves be more or less complex in nature.

We believe that the photochemical method of preparing ferric oxide smokes, should, at least in principle, avoid some of the complications arising in the previous methods. For example, the iron pentacarbonyl from which the aerosol is generated, may be uniformly distributed through the vessel as a vapour. With uniform and intense irradiation by ultra violet light, the formation of the aerosol may be accomplished uniformly throughout the entire volume, and hence the circumstances of condensation and coagulation are everywhere the same. The stirring, essential in other methods to obtain uniformity of distribution, must accelerate coagulation, and is practically dispensed with in this method. We are therefore able with certainty to produce as uniform an aerosol as possible. With sufficiently powerful illumination, strictly comparable aerosols of different concentrations can be prepared. Whilst arsenic dusts prepared thermally and under the same conditions deviated widely from one another in behaviour, according to their concentration, Fig. 2 shows that ferric oxide smokes of different concentration are not so differentiated ; the decrease in concentration and in number of particles are always in the same sense.

The two series of experiments cannot be strictly compared unrestrictedly, because of the different ranges of concentration. The smaller initial average weight of particle in the ferric oxide smokes, in comparison with that of the arsenic smokes, is characteristic of a highly unidisperse aerosol.

Whytlaw-Gray [20] has shown that ferric oxide smokes are not, unfortunately, suitable for general investigations, as they aggregate in a special way. Moreover, the course of the reaction expressed by the equation

$$4Fe(CO)_5 + 13O_2 = 2Fe_2O_3 + 20CO_2$$
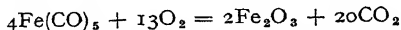
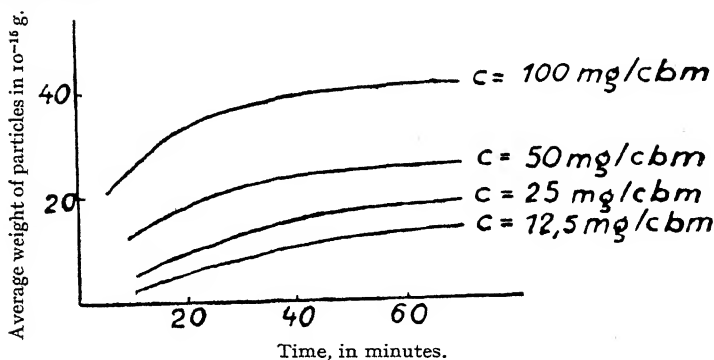is completely unknown, so that unforeseen complications may arise here.

FIG. 2.

Summary.

The behaviour of an aerosol will be decisively affected by the chemical and physical conditions prevailing during preparation, particularly in regard to the form and size of the particles formed. Relatively finely divided and approximately unidisperse systems have been obtained in different and reproducible ways, in all of which, however, there are some imperfections, which have been discussed. No method of preparation, ideal in every respect, has so far been evolved. Further improvement in methods of preparation depending on a closer knowledge of the rapidly occurring process of condensation preceding the formation of particles of colloidal dimensions, seems to us important, if we are to penetrate further into the characteristics of areosols.

[20] Whytlaw-Gray, *J. Chem. Soc.*, 1935, 276.

GENERAL DISCUSSION.

Dr. N. Fuchs (*Moscow*) (*communicated*) : In the work of Urasovski and Kusmenko,[1] the dispersity of NH_4Cl smokes formed by volatilisation in different media was compared, the number of particles per c.c. in 30-minute old smokes being

Medium.	Air.	Methane.	Methyl Alcohol.	Ethyl Alcohol.	Propyl Alcohol.	Benzene.
Number of particles per c.cm. . .	$1·0 \times 10^6$	$1·5 \times 10^6$	$2·5 \times 10^6$	$3·0 \times 10^6$	$0·5 \times 10^7$	$0·8 \times 10^7$

[1] Urasovski and Kusmenko, *J. Physic. Chem.* (Russian), 1935, **6**, 896.

As the weight concentration of smokes was very large (2 grams per cubic meter) they must have been very highly coagulated by the time they were examined and the results obtained can be interpreted as due chiefly to the different rate of coagulation in these media. The above figures show a complete parallelism with the diffusion coefficients of the media.

The same authors studied also the effect on the dispersity of smokes caused by the small admixture of some easily adsorbed vapours to the air in which they are formed. Only highly coagulated smokes were again examined. The most striking effect was observed with the admixture of phenol vapours, which markedly increased the dispersity of some smokes (NH_4Cl) and decreased that of others (MgO). We agree completely with Stumpf and Jander that this effect should not be attributed to the change in the effectiveness of collisions between the particles caused by the adsorbed layer. Most likely this layer causes a change in the size and form of the primary crystals,* and consequently in the structure of the aggregates formed from them. It would be very desirable to repeat these experiments, but adding the phenol vapours not before but after the formation of the smoke, as Stumpf and Jander have quite justly remarked.

The charging of the walls of the smoke-chamber (p. 1050) will not lead to any stabilisation of an unipolarly charged smoke. If all the walls are charged to the same potential there will be no field whatsoever inside the chamber. If the potential is different—the particles will move across the chamber and settle on one of its walls.

* *Cf.* crystallisation from solutions.

A SEDIMENTATION METHOD OF FINDING THE NUMBER OF PARTICLES IN SMOKES.

By R. Whytlaw-Gray, W. Cawood and H. S. Patterson.

The interpretation of the process of coagulation in smokes which has been previously put forward [1] depends upon the accuracy of counting in an ultramicroscope cell. We have shown that the Zsigmondy slit ultramicroscope gives an entirely erroneous estimate of the number of particles, and in consequence a special type of cell which we believe enables accurate data to be obtained was developed and used.[2] The unreliability of the slit ultramicroscope was first revealed by preliminary experiments on the sedimentation of smokes. This sedimentation method has been perfected and since it is free from certain objections which might be urged against counting with the special cell, the agreement which we have found serves to conform the validity of the previous conclusions on smoke coagulation.

Essentially the method consists in enclosing a known volume of smoke taken from the centre of the experimental smoke chamber between two strips of optically worked glass which form the top and bottom of a shallow box. The particles settle mainly on the lower plate and the number of particles can be counted when the deposit is suitably illuminated. Knowing the depth of the box and the area in which the count is made, it is easy to calculate the number of particles per c.c. of the smoke.

[1] Patterson and Cawood, *Proc. Roy. Soc.*, 1932, **136A**, 538.
[2] Nonhebel, Colvin, Patterson and Whytlaw-Gray, *Proc. Roy. Soc.*, 1927 **116A**, 540 ; Patterson, Whytlaw-Gray and Cawood, *ibid.*, 1929, **124A**, 502.

Sedimentation Method of Counting.

The enclosing of a known volume of smoke was accomplished by means of the device shown in Fig. 1.

The two glass plates A and B slide along the surface of a brass plate C perforated with a hole G. The glass plates are kept in position by sliding in grooves D, and are raised slightly above the level of the brass plate by strips of paper gummed to their edges. This device prevents abrasion of the highly polished surfaces by the brass. To the top of the plates are gummed strips of thin velvet ribbon to ensure that the plates fit tightly and move smoothly in the grooves. The plates originally occupy the position EF and are pulled simultaneously over the aperture into the position HK by means of strings. The small volume of smoke present in G is thus enclosed between the two glass plates and in standing sediments almost entirely on to the lower. The plates used are about 9 cm. long by 3 cm. wide with a bevel at the front end whilst the aperture G is oval, the size being about 1·2 cm. by 2·5 cm. Owing to slight turbulence and to diffusion, the deposit is apt to be irregular near the edges and it is therefore necessary that the area of G shall be large. In practice, however, the greater part of the deposit is perfectly uniform provided that
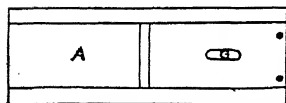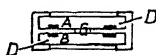

FIG. 1.

the cell is not too deep. Actually, we have used cells varying in depth from 2 to 10 mm. and within these limits the deposit is quite satisfactory though it is more uniform the shallower the hole. The brass holder carrying the plates was designedly of heavy metal to ensure thermal equilibrium and the absence of convection in the smoke during settling. We have termed the glass plates collector slides, and the brass cases in which they slide, collector slide holders.

After the deposit had settled, the slides were removed from the holder and examined microscopically, using a 16 mm. apochromatic objective N.A. 0·30 and a (×12) or (×20) eyepiece carrying a suitable squared graticule. The surface of the slide on which the particles had sedimented was illuminated from the front by a powerful focused beam of oblique light. The particles thus appeared as small bright diffraction discs on a black background. These operations were always carried out in a dust-proof box containing the microscope and slides, to avoid errors due to the deposition of floating impurities in the air. Counting presented no difficulty, the average number of particles per square of the eyepiece being obtained by enumerating a large number of fields in different parts of the deposit. Knowing the number of particles per square, the area of slide corresponding to the square, and the depth of the slide, the number of particles per c.c. can easily be found.

In the intense beam of illumination used the ordinary surface of glass even when optically polished shows numerous imperfections which simulate particles. By special polishing however, these can be almost entirely eliminated. In addition it is necessary that the surfaces before use shall be carefully cleaned. With certain types of glass this cleaning is not very difficult when the technique has been acquired and the surface when cleaned remains free from imperfections over long periods. With other

types of glass it appears practically impossible to rid the surface, even for short periods, of particulate matter. Thus on one hand the gentle friction of cleaning may produce such electrification of the surface that any particulate matter in the vicinity descends on the slides like a snowstorm, whilst on the other, particulate films due probably to moisture, may be almost impossible to eliminate or may be formed on standing for a short period. We wish to express our indebtedness to Sir Herbert Jackson, K.B.E., F.R.S., for kindly advising us as to the best types of glass to use, and also to Messrs. Hilger, Messrs Taylor, Taylor and Hobson, and Messrs. Cooke, Troughton and Sims, for obtaining the very special surfaces nesessary. Even under the best conditions, however, the cleaning of the slides calls for considerable skill. In all cases when the slides had been cleaned, they were examined before use in the manner described to ensure that they were free from deposits. Also after they had been exposed to a particulate cloud, the unexposed portion was scrutinised to see that the surface had not deteriorated. We found that the cleaning was best effected by a fine lawn cloth which had been treated beforehand with hot sodium carbonate solution and washed in pure water. The slightest trace of grease spoilt the surface immediately.

In studying the coagulation of a smoke, six or more of these collector slides were fixed to a suitable support in the centre of the smoke chamber and the slides were drawn at definite times by means of strings passing through corks in the side of the chamber.

Experimental Results for Coagulation.

This method has been applied to a large number of smokes and a considerable mass of data accumulated. A few typical results giving the

TABLE I.

Cadmium Oxide.			Cadmium Oxide.		
Time from Start, Min.	Number per c.c. × 10⁻⁶.	Particulate Volume × 10⁷.	Time from Start, Min.	Number per c.c. × 10⁻⁶.	Particulate Volume × 10⁷.
3	2·95	3·39	2	5·37	1·86
7	1·70	5·88	5	2·41	4·15
11·5	1·14	8·81	10	1·59	6·29
19·5	0·778	12·85	20	0·696	14·4
26·5	0·571	17·50	25	0·671	14·9
40·5	0·425	23·55	30	0·628	15·9
49·5	0·385	26·00	35	0·482	20·8
60	0·322	31·10	45	0·387	25·8
102	0·174	57·5	55	0·303	33·0

variation of number and particulate volume with time are given in Table I. The corresponding particulate volume-time curves are shown in Fig. 2.

It is evident that these coagulation curves are entirely analogous to those obtained with the special ultramicroscope cell. Actually a number of comparisons of two methods of counting have been made simultaneously on the same smoke. For this purpose, cadmium oxide smoke from a cadmium arc was used. The data obtained in two different experiments are given in Table II., whilst Fig. 3 shows the corresponding particulate volume-time curves.

It will be seen that there is a close agreement between the two sets of results. This is, perhaps, the more striking when it is considered that
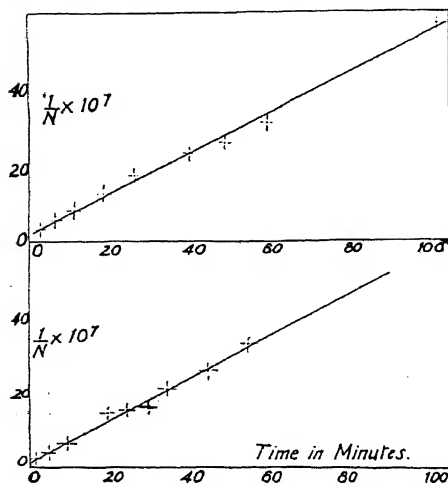
the two methods are subject to entirely different errors. It may be remarked that the examples given are those for smokes of a heterogeneous type which exhibit a large variability in the coagulation rates.

Counting by sedimentation has, however, its limitations. It is essential that the material used shall not be hygroscopic and obviously liquid particles which tend to wet the glass cannot be counted after settling on a slide. We have often watched the settling of tobacco smoke, of which a number of the particles are liquid, on a glass surface and it is interesting to see how rapidly the majority of the particles either disappear or diminish greatly in brightness when they come into contact with the glass. Further with a highly dis-

FIG. 2.

TABLE II.

	Counts with Cell.			Counts with Collector Slides.	
Time from Start in Minutes.	Number per c.c. × 10⁻⁶.	Particulate Volume × 10⁷.	Time from Start in Minutes.	Number per c.c. × 10⁻⁶.	Particulate Volume × 10⁷.
Experiment I.					
10	1·10	9·1	20·5	0·61	16·4
16	0·758	13·2	30·5	0·49	20·4
23·5	0·654	15·3	42·0	0·42	23·8
28	0·529	18·9	55·5	0·33	30·3
39	0·439	22·8	73·0	0·29	34·5
45·5	0·418	23·9			
50	0·372	26·9			
58	0·320	31·3			
62	0·325	30·8			
71	0·248	40·3			
86	0·230	43·5			
90	0·213	46·9			
Experiment II.					
7	0·909	11·0	8	0·92	10·9
12	0·990	10·1	24	0·47	21·3
17	0·629	15·9	43	0·33	30·3
22	0·553	18·1	62	0·24	41·7
27	0·481	20·8	84	0·21	47·6
31	0·412	24·3			
39	0·337	29·7			
46	0·345	29·0			
59	0·295	33·9			
73	0·218	45·8			
82	0·198	50·5			
95	0·168	59·4			
101	0·181	56·4			

perse smoke, especially in its early stages, all the particles may not be enumerated on account of the low intensity of the light scattered by the smaller units. In addition, a time correction of small but uncertain magnitude should be applied to these early points to allow for the coagulation taking place during sedimentation. Consequently, the collector slide counts for very fine smokes will be too low.

FIG. 3.

GENERAL DISCUSSION.

Dr. R. Lessing (*London*) asked whether the method was also applicable to dusts.

Professor F. G. Donnan (*London*) drew attention to the fact that the first observations on photochemically produced disperse systems in gases were made by Tyndall very many years ago. In fact, the famous " Tyndall beam " arose from this work.

Dr. F. T. Peirce (*Manchester*) said : The question seems to be whether there is real physical meaning in the zero of time on the coagulation curve. Is the extrapolation to zero made along the linear empirical relation of $1/n - t$, or in accordance with the theoretical expression for K ?

Dr. W. Cawood (*Leeds*), in reply, said : The method would be easily applicable to dusts of the size range down to the limits given.   We have successfully obtained a thick deposit with dusts of low concentration, by using collected slides of greater depth than those described.   This method is, of course, quite different from the ordinary method of sedimentation on to a cover glass, where the glass surfaces are not sufficiently perfect for oblique illumination to be used and with direct light the smallest particles are not counted.
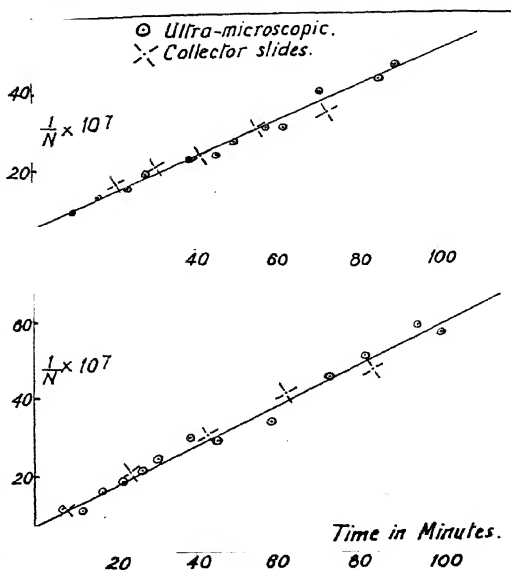
THE INFLUENCE OF PRESSURE ON THE COAGULATION OF FERRIC OXIDE SMOKES.

By W. Cawood and R. Whytlaw-Gray.

Jander and Winkel,[1] in a comprehensive research on ferric oxide aerosols, have shown that perfectly reproducible smokes can be obtained by the photochemical decomposition of dilute iron carbonyl vapour ($Fe(CO)_5$) in air.   They point out that these ferric oxide smokes exhibit, in their early stages at least, a high degree of homogeneity and that the

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[1] *Kolloid Z.*, 1933, **63**, 5.

method provides a ready means of studying the coagulation of aerosols at varying pressures.

The results, however, which they obtained for the course of coagulation at atmospheric pressure differ markedly from those of the majority of smokes we have examined and we attribute this difference to the method employed for counting the number of particles. Moreover, the experiments they carried out at pressures below atmospheric, though showing clearly that coagulation takes place at a greater rate, did not give any indication of the form of the coagulation curves. For these reasons a further study has been made of the ferric oxide aerosols which are formed by the very elegant method of photochemical decomposition discovered by these two investigators.

Experimental.

In any research on the coagulation of smokes the essential measurement is the determination of the change with time of the number of particles per unit volume. For this purpose counting with the Zsigmondy slit ultramicroscope is often used, but this method, as we have shown, is unreliable when applied to smokes and may frequently lead to erroneous results.[2] In the experiments to be described we have therefore used the improved form of counting cell and the method which experience has shown to be reliable.[3]

Our arrangements have been criticised by Jander and Winkel [4] but we wish to point out that our method has been tested by comparison with two other independent methods of counting, *viz.*: the modified Aitken method developed by Green [5] and a sedimentation method described in this discussion. All three methods agree closely. We believe, therefore, that our system of counting particles is reliable.

The smokes were dispersed in a similar manner to that used by Jander and Winkel.[1] A thin glass capsule containing a solution of iron carbonyl dissolved in anhydrous ether was broken by means of an electromagnetic arrangement, at the centre of a 20 litre pyrex globe containing filtered air. The flask was radiated by placing it upon a rotating table between two 10 ampere arcs for six minutes. It was then connected with the counting cell and observations were made at suitable intervals of time.

The first experiments were carried out at atmospheric pressure, in order to test the reproducibility of the smokes. Three smokes of equal weight concentrations (16·5 mgms. Fe_2O_3 per cubic metre) were counted. When the results were plotted in the usual manner of particulate volume against time, straight lines were obtained in each case, within the limits of experimental error. Plotted in this manner each graph extrapolated back to near the origin and the slopes of the three agreed closely, the

following values for the coagulation constant K in the equation $\dfrac{1}{n} - \dfrac{1}{n_0} = Kt$ being obtained.

	Concentration.			$K.$ (cm.^{3}/min. $\times$ 10^7).
1.	16·5 mgms. per cubic metre			0·408
2.	,,	,,	,,	0·407
3.	,,	,,	,,	0·399

The experimental points of one of the smokes are reproduced in Fig. 1. These results show that the smokes are highly reproducible, and that

[2] *Proc. Roy. Soc., A* 1927, **116**, 540.
[3] Patterson, Whytlaw-Gray and Cawood, *Proc. Roy. Soc., A* 1929, **124**, 502.
[4] Schwebstoffe in Gasen, 1934, pp. 16 and 44.
[5] *Phil. Mag.*, 1927, **4**, 1046.

the coagulation curves are very similar to those which we have obtained previously. They do not, however, agree with Jander and Winkel's graphs for smokes of a similar concentration, which exhibit a distinct curvature and show a much higher number concentration at corresponding times. It may be noted that earlier counts made by one of us with a Zsigmondy slit ultramicroscope and known to be erroneous, approximate closely to their results.[6]

Coagulation curves at pressures below atmospheric were obtained in the following way. After filling the 20 litre globe with filtered air and introducing the thin glass capsule containing t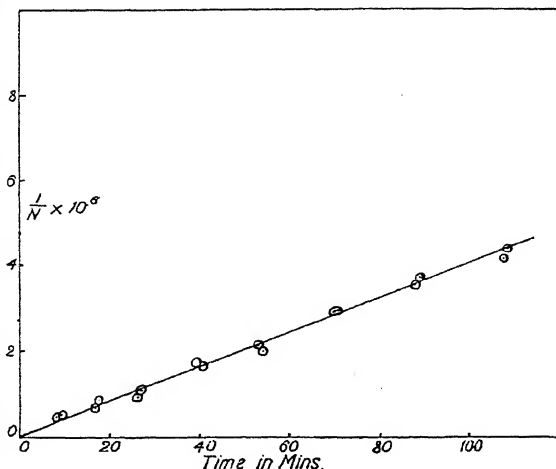he ethereal solution of iron carbonyl of the standard concentration, the pressure was reduced to a suitable value. The capsule was then broken and the flask radiated. Coagulation was allowed to proceed for a definite period and then filtered air was admitted until atmospheric
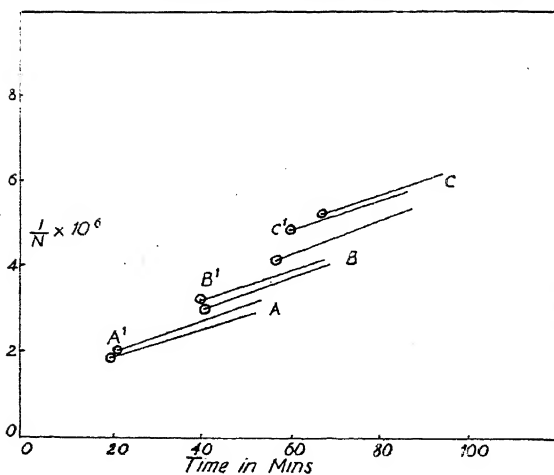

FIG. 1.

pressure was reached. The smoke was then thoroughly mixed and counts taken in the usual manner over a period of about half an hour. The extrapolation of the graph so obtained back to the time when the air was admitted gave the number of particles per c.c. to which the smoke had coagulated at the reduced pressure. This procedure was carried out a number of times at the same initial pressure, allowing different

FIG. 2.

intervals to elapse before the pressure in the flask was brought up to atmospheric. In this way a number of points was obtained on the coagulation curve at the low pressure. The accuracy of this method

[6] *Proc. Roy. Soc., A* 1922, **102**, 601.

depends upon the degree of reproducibility of the smokes, but the data obtained from different experiments were perfectly consistent and showed no indication of irregularity. The method will be clear from Fig. 2. Thus the lines A, B and C represent the experimental graphs obtained after letting air into the globe. Thes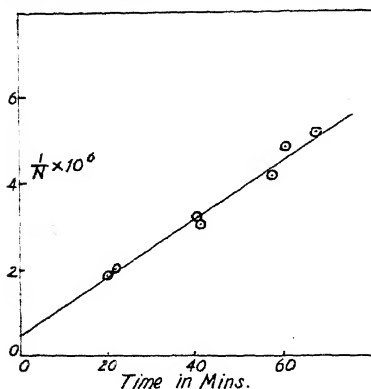e all proved to be straight lines parallel to the coagulation graph at atmospheric pressure. A^1, B^1 and C^1 are the points obtained by extrapolating the experimental graphs back to the time when the pressure in the flask was brought to atmospheric. It may be noted that there is very little error in this as the extrapolation is only of the order of two or three minutes. The points A^1, B^1, and C^1 were then plotted as in Fig. 3, showing the course of the coagulation at the lower pressure. The actual points plotted in Figs. 2 and 3 correspond to the results taken at 400 mm. pressure. The graph at 200 mm. pressure was obtained in a precisely similar manner. In Fig. 4 are reproduced the coagulation curves at 760 mm., 400 mm. and 200 mm. pressure.

FIG. 3.

These experimental graphs show several interesting features. They confirm Jander and Winkel's observations that the rate of coagulation increases markedly as the gas pressure falls. On the other hand, the relationship between the number of particles present after the same interval of time in systems coagulating at different pressures does not, as these observers affirm, appear to vary linearly with pressure.

The graphs, over the time range considered, are straight and when extrapolated to zero time do not start from the same point. This would indicate that at the lower pressure a smaller number of particles is formed initially than at the higher pressures. With stearic acid it has been shown [3] that in air at normal pressure the number of primary particles must be very large and of the order of 10^{12} per c.c. This

FIG. 4.

value is in approximate agreement with a direct experimental determination made by Fuchs and Oschman, [7] in which they found the initial number per c.c. about 10^{11} and the radius 1·2 to 1·5 10^{-6} cm. in a sulphuric acid aerosol at atmospheric pressure.

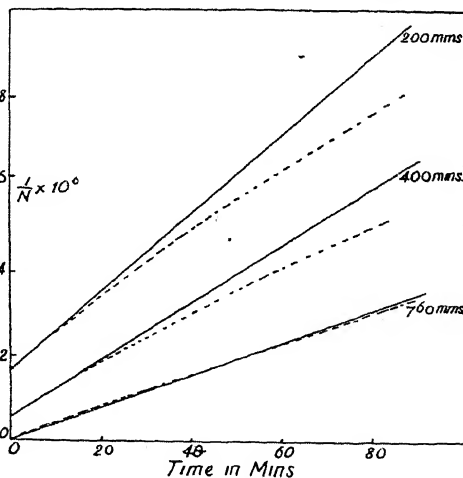Our graphs for Fe_2O_3 at atmospheric pressure also indicate a very

[7] *Acta. Physica chimica U.R.S.S.*, 1935, III, 61.

high initial number and consequently a small value for the radius of the primary particle, whilst those for the 200 mm. pressure show that coagulation must start from much larger units.

Although little is known directly about the early stages of smoke formation it is probable that nuclei are first formed in the supersaturated vapour and that a proportion of these grow rapidly by condensation to primary particles. On this view the results we have obtained indicate either that the number of nuclei present in the initial stages changes rapidly with pressure, or that the number of nuclei is constant but the proportion developing into primary particles becomes smaller as the air pressure falls. The particles in the Fe_2O_3 smokes formed at atmospheric pressure should hence consist of aggregates of amicroscopic or ultramicroscopic primaries whilst those formed at low pressures should be composed of markedly coarser units.

To test this point a microscopic examination was made of the deposits obtained from two ferric oxide smokes of the same weight concentration, one of which had been formed and allowed to coagulate for three hours at atmospheric and the other at a pressure of 200 mm. The deposits were obtained both by direct sedimentation on to microscope cover slips and by thermal precipitation. They were examined with a 2 mm. Leitz apochronatic oil immersion objective and illuminated by transmitted light of short wave-length. A marked difference in the character of the units composing the aggregates was at once apparent. In both cases chain-like complexes were predominant but the units in those formed at the higher pressure were beyond the limit of microscopic resolution and were indeed extraordinarily difficult to observe at all, whilst those in the aggregates formed at the lower pressure were very distinctly larger and easily observable.

This result confirms in an entirely satisfactory manner the explanation given of the different starting-points of the graphs in Fig. 4. The effect of gas pressure on the size of the particles is also supported by results obtained by Kohlschutter with smokes of metallic oxides dispersed from an arc in air at various pressures.[8]

The general form of the three graphs and their theoretical significance now calls for some discussion.

Discussion.

It has been shown that the coagulation of various types of smoke is in conformity with the theoretical expression of Smoluchowski, if certain modifications are inserted to take account of the heterogeneity and the mobility of the smoke particles.[3] Thus the coagulation of a smoke containing about equal numbers of particles of range of radius of about 1 to 7 is given by

$$-\frac{dn}{dt} = \frac{4}{3}\frac{RT}{\eta N}\left(1 + \frac{Al}{r}\right) \times 1.25, \quad \text{where } n = \text{number of particles per c.c.,}$$

$n_0 = $ initial number of particles per c.c.,

$l = $ mean free path,

$r = $ radii of particles,

$\eta = $ viscosity of gas.

and consequently

$$t = \frac{\sigma - \sigma_0}{\frac{4}{3}\frac{RT}{\eta N}\left(1 + \frac{Al}{r}\right)1.25}$$

$$\sigma = \frac{1}{n},$$

$$\sigma_0 = \frac{1}{\eta_0}.$$

[8] Kohlschutter and Ehlers, *Z. Electrochemie*, 1912, **18**, 373.

The factor 1·25 is the heterogeneity factor and has this value for the particular size range mentioned above. Since r is the average value of the radius it will obviously depend upon the age of the smoke and may be calculated as follows.

If the size range is 1 to 7

then $$\frac{n}{7} \cdot \frac{4}{3}\pi\rho(x^3 + (2x)^3 + \ldots (7x)^3) = M \quad 10^{-9}$$

where n is the number of particles per c.c., ρ their density, x the radii of the smallest and M the concentration of the cloud in mgms. per cubic metre.

Therefore the average radius r of the particles will be

$$r = 4x = 4\sqrt[3]{\overline{M \cdot 10^{-9}}}$$

It is interesting to note that the average radius calculated in this way is only about 0·81 of that calculated by assuming that all the particles are of equal radii.

The above expression has been applied to our smokes and the dotted lines in Fig. 4 give the theoretical curves so calculated. The only effect of the reduction of the pressure upon the equation is to increase the value of l, the mean free path of the gas.

It will be seen that the theoretical curve calculated for the smokes at atmospheric pressure is in good agreement with the experimental curve. The agreement, however, is not at all good at the lower pressures. This is due to the fact that the rate of coagulation of any two particles of radii r_1 and r_2 is proportional to the factor $\left[\left(1 + \frac{Al}{r_1}\right) + \left(1 + \frac{Al}{r_2}\right)\right]$ The change of this term with pressure is not constant for different values of r_1 and r_2, consequently the size distribution and heterogeneity of the smokes must alter quite appreciably with change of pressure, even though the mass concentration is kept constant. Thus we should not expect the equation which agrees with results taken at atmospheric pressure to agree with those at reduced pressure unless allowance can be made for the alteration in size distribution.

It must be borne in mind when considering these ferric oxide aerosols that on account of the chain-like character of the aggregates in the later stages of coagulation, the particles even in the earlier stages may deviate considerably from the spherical in form, and the applicability of the Smoluchowski theory modified in the above manner to these may well be questioned. We are led, therefore, to the conclusion that though this theory provides a useful qualitative hypothesis for the explanation of the kinetics of the coagulation of aerosols in general, it cannot be expected to express quantitatively the coagulations of more complex systems such as these ferric oxide smokes, although for certain systems, such as stearic acid, the correspondence between experiment and theory is very close.

Summary.

A study has been made of the coagulation of ferric oxide aerosols dispersed by the photochemical decomposition of iron carbonyl in presence of air at pressures of 760, 400, and 200 mm. The particulate volume

graphs are found to be linear but their slope becomes steeper as the pressure falls.

The values of σ_0 differ markedly in the three cases and indicate that the smokes formed at lower pressures start from larger primary particles.

Microscopic examination of the aggregates confirms this conclusion. The limitations of Smoluchowski's theory when applied to smokes of this type are discussed.

GENERAL DISCUSSION.

Mr. C. H. Bosanquet (*Billingham*) said : The fact that the straight lines showing $1/n$ in terms of t at different pressures do not cut the axis of zero time at the same point may be due to the l/r term in Smoluchowski's equation being predominant in the initial stages when r is very small. This would cause pronounced curvature of the lines near the origin, the effect being more marked at the lower pressures. Comparison of the values of n after equal lapses of time would not then give directly comparable results, accounting at least in part, for different mean particle sizes being found.

Dr. W. Cawood (*Leeds*) said in reply : If the theoretical curves shown by the dotted lines in Fig. 4 are calculated by assuming $\sigma_0 = 0$, then the l/r correction will not give the required curvature. In practice the curves for the low pressure results, calculated with this assumption are more or less parallel to those given in Fig. 4, but start from zero. The only way to obtain an even approximate agreement between theory and experiment seems to be to assume the initial number obtained by a linear extrapolation of the experimental results.

The effect of the l/r correction may be shown approximately by solving the equation given in the paper for σ_0.

Thus
$$\sigma_0 = t \cdot \frac{4}{3} \frac{RT}{\eta N} \left(1 + \frac{Al}{r}\right) - \sigma$$

assuming the experimental values for σ and t. Since at the low pressures the experimental points do not lie exactly along the theoretical curve, the values for σ_0 will not be the same for the different experimental values of σ and t, but the values of σ_0 so obtained are not widely different from those obtained by a linear extrapolation.

The empirical correction for radius in Harper's theory certainly tends to make the curvature smaller, but this correction, which incidently appears to be given more rigidly by Fuch's treatment of Smoluchowski's equation only applies to particles smaller than about 3.5×10^{-6} cms. radius. In our clouds the particles are larger than this after two or three minutes and consequently the extrapolation would not be greatly changed.

Dr. W. R. Harper (*Bristol*) said : The extrapolation of the particulate volume/time graph as a straight line to zero time is inconsistent with the variation of the coagulation coefficient for small particle size implied by the formula assumed in the paper, and though the variation is less on my own theory, it would still be sufficient to invalidate any conclusions concerning the existence of primary particles drawn from this extrapolation.

Mr. A. G. Grant (*Darlington*) said : In the formation of a particle of, say, 10^6 molecules from a condensing vapour, there must first be a union of two or more molecules, this first group growing until it reached the size of Whytlaw Gray's " primary particle." Although considerations of coagulation apply to these " primary particles," further extrapolation of the curves showing particles size against time, should lead to a bi-molecular particle, unless there is some discontinuity. In other words, either the " primary particle " is a somewhat arbitrary unit, or it represents a point of discontinuity.

Dr. R. Lessing (*London*) suggested that the differences observed at varying pressure may be due to the chemical mechanism of the decomposition of iron carbonyl rather than to the behaviour of its vapour. In

the commercial production of nickel from its carbonyl slight variations in the temperature of decomposition changed the structure of the fresh metal bloom deposited on the old nickel pellets. Dewar [1] has shown the influence of pressure on the temperature of decomposition of nickel carbonyl.

Mr. C. F. Goodeve (*London*) said : What is the exact meaning of the term " primary particle," as used in this paper and the introductory paper. The term seems to imply some clearly defined intermediate state between the original molecular dispersion and the colloidal one obeying a bi-molecular coagulation law. The extrapolation to zero time does not seem to be very useful, because it depends on a too accurate measurement of time and definition of the starting-point.

It is necessary also to consider the mechanism of the formation of ferric oxide smokes. The question as to the necessity for condensation nuclei before the formation of smokes or fogs has often been discussed. I am attempting to build up a quantitative theory based on initial clustering of the molecules in a supersaturated gas—a theory somewhat on the lines suggested by Volmer.[2] It is now possible to determine approximately the heat of formation of clusters of 2, 3, 4, etc., molecules, knowing only the latent heat of evaporation of one molecule from a flat surface of the solid or liquid substance. As a rough approximation, the energy required to separate two molecules in contact in a cluster, is one-tenth of that required to remove one molecule from a flat surface. The energy required to remove one molecule from a triple cluster is about twice this and, from a quadruple cluster, less than three times. The latent heat of evaporation of ferric oxide from a crystal is probably not known, but would be greater than 100,000 Cals. per gram molecule. This means that, if two ferric oxide molecules collide and are relieved of their excess energy by radiation or by collision with gas molecules, they would require about 10,000 Cals. per gram molecule energy to break them apart. This amount of energy could rarely be obtained at room temperature, where the average energy per degree of freedom would be a few hundred Calories. Double clusters, once formed, would grow very rapidly to larger clusters and eventually to smoke particles. It is seen therefore, that, in the case of ferric oxide, it is entirely unnecessary to have nuclei present before condensation could occur.

These considerations, however, do not apply to super-saturated water vapour. Two-molecule clusters are held together by only about 1000 Cals. and would be very readily broken up on collision with gas molecules.

From these considerations it is very difficult to see how, with ferric oxide, any discontinuity in the condensation process could occur. The building up of clusters and their coagulation to larger particles would be a smooth continuous process, following approximately the considerations given.

Mr. G. W. Slack (*Leeds*) said : The number of *primary particles* is dependent upon the rate of formation of nuclei and upon their rate of growth when formed. The former (in the case of smokes of Fe_2O_3 and similar substances of vanishingly low vapour pressure) is probably equal to the number of molecular collisions and will therefore be independent of the nature of the medium, whilst the latter (being governed by the diffusion of vapour to the surface of these nuclei) is assisted by the increased mobility due to the lower pressure in the case of the experiments at 200 mm. and 400 mm. The combined result is that fewer nuclei have time to be formed in the short interval before supersaturation is relieved.

Professor Dr. G. Jander and Dr. K. E. Stump (*Greifswald*) (*communicated*) : This work emphasises the great importance of such photochemical reactions in the investigation of those aerosols in which the readily volatile material forms a substance of very low vapour pressure and a gaseous product, *e.g.* by the interaction of the oxygen of the air in

[1] *J. Chem. Soc.*, 1904, **86**, II., 488.
[2] M. Volmer, *Electrochem.*, 1929, **35**, 555.

the photolysis of iron pentacarbonyl vapour to produce iron oxide, dust and carbon oxides.

The authors' results agree with those of our own recent work, qualitatively but not quite quantitatively, therefore fuller quantitative investigation of this whole complex question is needed; we shall therefore repeat the more fundamental measurements with every precaution to avoid experimental error.

Dr. N. Fuchs (*Moscow*) (*communicated*) : The chief difficulty in the investigation of the formation of aerosols lies in strictly separating the two quite different processes involved, *viz.*, the condensation of vapours and the coagulation of the primary aerosol. This may be done either by " fixation " of the primary aerosol by very strong dilution or, as done by Cawood and Whytlaw-Gray, by extrapolation of the numbers of particles per c.c. found in a coagulating aerosol to the moment of its formation. The second important obstacle (the difficulty of obtaining uniform supersaturation throughout the whole volume of the vapour) is completely removed in the photochemical method of smoke formation used in this work. We could therefore say that the experiments of Cawood and Whytlaw-Gray were made under ideal conditions except for the relatively long (6 min.) time spent in the formation of the smoke.

The chief result of these experiments (the increasing of the dispersity of the primary smoke with the air-pressure) can be interpreted unequivocally from the view-point of the modern theory of nuclei formation in supersaturated systems.[3] Since, according to this theory, the number of nuclei formed in unit of time must be independent of the air-pressure, the result mentioned can only be caused by different rate of growth of the nuclei. For particles considerably smaller than the mean free path of the gas-molecules, the rate of growth is also independent of the air-pressure : [4] a perceptible difference in the rate of growth at different pressures will begin only when the growing particles have reached the size of about 10^{-6} to 10^{-5}] cm. Henceforth they will grow the faster, the larger the co-efficient of diffusion of $Fe(CO)_5$ vapour, *i.e.* the less the air-pressure.

Dr. W. Cawood (*Leeds*) said : With reference to Mr. Goodeve's suggestions as to the formation of condensation nuclei from the molecules of ferric oxide itself, I am in complete agreement. Indeed, we meant to imply such nuclei in the paper.

The difference between condensation from supersaturated vapour and coagulation, I consider to be quite sharp and defined. In condensation, the molecules of the supersaturated vapour collide and an amount of energy equivalent to the energy of formation of the solid is dissipated, a homogeneous primary crystal or particle being thus formed after a sufficient number of molecules have condensed. In coagulation, however, we have the case of two of these primary crystals colliding. They do not in general form one crystal (except in the rare case of the correct edges coinciding and even then an adsorbed layer of gas might keep them separated) nor do they dissipate energy because they are already in the solid phase. This type of coagulation would form the loose-chain-like aggregates which we observed.

Thus, we see that whilst condensation builds up homogeneous particles or crystals, coagulation (in the case of solids) forms aggregates. Moreover, the first process, with a substance like ferric oxide would be much faster than the second. It appears very likely therefore, that in the formation of such smokes, primary crystals are really formed initially and almost instantaneously by condensation, whilst coagulation is a secondary process.

Professor R. Whytlaw-Gray (*Leeds*), in reply, said : Little is known about the initial stages in the formation of smoke. As Mr. Goodeve has pointed out, in systems of non-volatile particles such as those of ferric

[3] Becker and Döring, *Ann. Physik.*, 1935, **24**, 719.
[4] Fuchs, *Physik. Z. d. Sovjetunion*, 1933, **4**, 481.

oxide it is very unlikely that any of the small molecular clusters first formed split up again, as is the case with volatile systems, and it might be contended that the process is a continuous one of progressive aggregation from the molecular to the particular state.   If this were so, a freshly formed smoke should always be heterogeneous and contain all sizes of particles and this heterogeneity should persist during coagulation, giving an extended size distribution of the Smoluchowski type.   On this view I agree that the term " primary particle " would be difficult to define.   It appears to me, however, that the process is not a continuous one.   As a result of molecular encounters a certain number of larger clusters will be formed which contain sufficient molecules to give crystalline units or super-cooled droplets.   These will then act as nuclei or centres of condensation for the molecules and smaller clusters, and the system formed finally will be approximately homogeneous.

This apparently is what happens in the formation of a gold sol ; primary particles of crystalline gold are formed and, as Zsigmondy and others have shown, the process is dependent on the rate of formation of nuclei and the rate of crystallisation.

If this interpretation can be applied to a smoke, compact particles, often crystalline, will first be formed, these are the primary particles. These will immediately begin to coagulate, and will form later the complexes of loose or chain-like structure which we see in the microscope.   The units composing these complexes can, in the case of many smokes, be separated by peptisation with suitable solutions to form hydrosols (as Kohlschütter has shown) but the size of the particles in these has not been determined.

Coagulation, then, is the linking together of compact solid units, which may be crystalline or amorphous, and seems to me to be essentially different from the processes of molecular condensation by which the smoke is formed.   Probably the two processes go on simultaneously to some extent and in the early stages the multiple particles formed by coagulation may be cemented together by condensation.

THE MOVEMENT OF DUST OR SMOKE PARTICLES IN A TEMPERATURE GRADIENT.

By W. Cawood.

The existence of a dark space round a hot body in a smoke or dust was first observed and studied by Aitken.   Since then the size of the dark space and its relations with temperature difference and pressure have been studied by various observers, but no quantitative explanation of the phenomena has been put forward.   The effect is almost certainly not due to the radiant energy of the body, for the particles of dust or smoke are in continuous rotation and consequently have an even surface temperature.   Also there appears to be no reason why the dark space should have a sharp edge if the phenomenon be due to radiation. Finally, quite a strong effect may be observed at the edge of a solid body only about 10° C. higher than the surrounding air, when the radiation would be extremely small, and moreover the dark space does not appear to be dependent upon the nature of the solid surface.

A consideration of the mechanism of the conduction of heat from solid bodies to gases appears to afford a clue to the true explanation of the effect.

It is well known that when a solid body is heated by a flame, there is a sharp temperature gradient near to the surface of the solid.* Thus, an old experiment is to boil a kettle with a piece of paper stuck on the bottom. The paper does not char, showing that the hot gas molecules do not actually reach it. The dark space may be observed if the velocity of the flame is not too great, and may reach a thickness of about 2 to 3 mm. If the upward velocity of the flame is increased the dark space gets thinner, but never entirely disappears. This one would expect, because the temperature gradient near to the cold surface is set up at a velocity of the same order as the molecular velocities, whilst the blast velocity of burning gas is much smaller.

It is interesting to note, however, that if a smoky flame is used, although the dark space may be observed with ease, the solid particles of carbon are projected through it and deposited on the cold surface, the reverse effect of the dark space round a hot body in a smoke.

This affords a clue to the latter phenomena, *i.e.*, that there is a force which tends to move small particles down a temperature gradient. In other words, that smoke particles will tend to be repelled by a hot body and be attracted by a colder one.

Let us now consider the conduction of heat between solids and gases in greater detail. Consider an infinite flat plate at a temperature T_1 and a gas below it at a lower temperature T_2, and from the foregoing let us assume that the total temperature gradient is contained in a small strip of gas near to the hot plate. If now there were no convection currents, that is, mass movements of the gas, then if we take any small surface in the temperature gradient

where $N_1 N_2$ are the number of molecules per cubic centimetre on each side of the surface with components perpendicular to the surface, and c_1, c_2 are their average velocities corresponding to the difference of temperature dT. This of course is the relationship which Knudsen[1] finds to hold at low pressures and through small apertures.

Consequently

$$\frac{N_1 c_1^2}{N_2 c_2^2} = \frac{c_1}{c_2}$$

$$\therefore \frac{p_1}{p_2} = \sqrt{\frac{T_1}{T_2}}$$

and

$$\frac{N_1}{N_2} = \sqrt{\frac{T_2}{T_1}}$$

If, then, there were no convection, the pressure of the gas near the hot plate would be higher than at distances more remote. In practice, no pressure differences are to be detected under a horizontal hot plate even with an accurate oil gauge. This is because convection is present and the above assumptions do not hold good. As Knudsen[1] has shown, the pressure difference can be observed and indeed confirms the square root law, only if convection is obviated by connecting the two vessels containing gases at a different temperature by means of tubes of radius of the same order as the mean free path of the gas.

* This is known as the skin effect in engineering. Measurements of the heat conductivity from gases to solids appear to give the gradient as about one-tenth of a millimeter wide.

[1] M. Knudsen, *Ann. Physik*, 1909, **28**, 75, 999 ; 1910, **32**, 809.

It must be emphasised, however, that although convection destroys the pressure differences it does not destroy the temperature gradient. As is shown by the flame experiments, the gradient may be made steeper by the quick mass movements of the gas, but is never entirely destroyed.

Let us now consider a small cylinder of gas in the temperature gradient, of length about twice the mean free path of the gas. If the cylinder has a sufficiently small radius, convection currents will not affect the movements of the molecules parallel to the axis of the cylinder, for the perpendicular velocity gradient of a convection current is not continuous, but must vary in steps of the order of magnitude of the mean free path of the gas. Consequently the velocity on both sides of such a cylinder will be approximately equal. Such a cylinder will therefore move bodily in the current, but the temperature difference between the ends will be the same, and apart from the average temperature being altered, the cylinder will otherwise be unaffected. Consequently in this very small cylinder one would expect Knudsen's laws to be obeyed.

Consider now a smoke or dust particle in the middle of the cylinder. It will be bombarded by gas molecules moving in all directions but it is only necessary to consider the bombardments due to molecules moving perpendicularly to the plate, and if F is the force per unit area parallel to the plate then the total force on the one side of a spherical particle is

$$\int_0^{\pi/2} F \cdot 2\pi r^2 \sin\theta \cdot \cos\theta \cdot d\theta$$
$$= F \cdot \pi r^2.$$

The force on the spherical particle due to the bombardment of the gas molecules may now be calculated in a similar manner to that in which Einstein [2] calculated the force on a vane radiometer.

Thus $\frac{1}{6}N_1 c_1(\pi r^2)$ molecules will collide with the particle on one side and $\frac{1}{6}N_2 c_2(\pi r^2)$ on the other, where N and c have their usual significance. The difference of velocities of the molecules accounts for the heat flow.

Thus the heat flow if the particle was not there

$$= (\pi r^2)f = \tfrac{1}{6}N_1 c_1 \cdot (\pi r^2) \cdot \frac{mc_1^2}{2} - \tfrac{1}{6}N_2 c_2(\pi r^2) \cdot \frac{mc_2^2}{2}$$
$$= \tfrac{1}{6}N_1 c_1(\pi r^2)\left[\frac{mc_1^2}{2} - \frac{mc_2^2}{2}\right] \quad . \quad . \quad . \quad . \quad (1)$$

where $f =$ heat or energy flow per unit area;
    $m =$ mass of gas molecules.

If c_1 and c_2 are the velocities appropriate to the temperatures at the place of the last collision, i.e., at the ends of the cylinder then

$$\tfrac{1}{2}mc^2 = \tfrac{3}{2}RT$$

and

$$\tfrac{1}{2}m(c_1^2 - c_2^2) = -\tfrac{3}{2}R \cdot \frac{dT}{dx} \cdot 2L$$

where $L =$ mean free path of gas.

$$\therefore f = -\tfrac{1}{2}N_1 c_1 \cdot R \cdot \frac{dT}{dx} \cdot L \quad . \quad . \quad . \quad . \quad (2)$$

[2] A. Einstein, *Z. Physik*, 1924, **27**, 1.

If now we consider the smoke particle then there will be excess of momentum (k) away from hot plate

i.e.,
$$k = \tfrac{1}{6}N_1 c_1(\pi r^2) \cdot mc_1 -$$
$$= \tfrac{1}{6}N_1 c_1(\pi r^2)[mc_1 - mc_2] \qquad . \qquad . \qquad . \qquad . \quad (3)$$

and if the impulse due to recoil is neglected then $k =$ force on particle

$$\therefore k = \frac{\pi r^2 f}{c} \text{ (from (1) and (3))}$$

$$= - \tfrac{1}{2}N_1 R \cdot \frac{\mathrm{d}T}{\mathrm{d}x} \cdot L \cdot \pi r^2 \text{ (if } c = \frac{c_1 + c_2}{2} \text{ and } c \text{ is very nearly } = c_1)$$

$$= - \tfrac{1}{2}p \cdot \frac{\mathrm{d}T}{\mathrm{d}x} \cdot \frac{L}{T} \cdot \pi r^2 \quad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \quad (4)$$

If a smoke particle moves under a constant disturbing force k, however, we have

$$k =$$

where $V =$ velocity; $\mu =$ viscosity of gas; $A =$ constant.
Also as the edge of the dark space acts as a semi-permeable membrane then the smoke as a whole exerts an osmotic pressure on the edge of the space equal to $\frac{RT}{N} \cdot n$ where $n =$ number of particles per 22·2 litres. For one particle this is the component of the Brownian motion on the edge and is therefore $\frac{RT}{N}$ and the force of one particle on the space is $\frac{RT}{N} \cdot \pi r^2$. Consequently

$$\tfrac{1}{2} \cdot p \cdot \frac{\mathrm{d}T}{\mathrm{d}x} \cdot \frac{L}{T} \cdot \pi r^2 = \frac{6\pi\mu r V}{\left(1 + \frac{AL}{r}\right)} + \frac{RT}{N} \cdot \pi r^2$$

$$\therefore V = \frac{\left(\tfrac{1}{2} \cdot p \cdot \frac{\mathrm{d}T}{\mathrm{d}x} \cdot \frac{L}{T} \cdot \pi r^2 - \frac{RT}{N} \cdot \pi r^2\right)}{6\pi\mu r} \cdot \left(1 + \frac{AL}{r}\right)$$

The velocity given by the above equation is the velocity in the small cylinder of gas which we have considered. If, as actually happens, there is a convection current towards the plate, the actual velocity will be reduced, because the cylinder will be moving bodily in the current and if the convection is fast enough the dark space should not be observed at all. As will be seen later this is confirmed by experiment. Also, although the velocity appears to be proportional to the radius of the particle this is not actually the case, for the fundamental assumption is that the radius should be of the same order as the mean free path of the gas (*i.e.* about 10^{-5} cms.). If the radius is much larger than this, then if the dust-free space is due to molecular bombardment, the force will be destroyed by the convection effects and very large particles ought not to move away from the hot body. According to other observers this actually is the case.[3]

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[3] H. H. Watson, *this discussion.*

If the temperature gradient is linear over the region of the dark space, then the time taken for a particle to move from the plate to the edge of the dark space may be calculated as follows.

From the last equation (neglecting the $\frac{RT}{N} . \pi r^2$ term)

$$V = \frac{\mathrm{d}x}{\mathrm{d}t} = \frac{K}{T}$$

where

$$K = \frac{\frac{1}{2}p . \frac{\mathrm{d}T}{\mathrm{d}x} . L . r}{6\mu} . \left(1 + \frac{AL}{r}\right)$$

and if $\frac{\mathrm{d}T}{\mathrm{d}x}$ is constant

then

$$T_x = \frac{\mathrm{d}T}{\mathrm{d}x} . x + T_G$$

where T_G is temperature of gas.

$$\therefore \frac{\mathrm{d}x}{\mathrm{d}t} = \frac{K}{\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right) . x + T_G}$$

$$\therefore t = \left(\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right) . \frac{x^2}{2} + T_G . x\right) . \frac{1}{K}$$

$$= \frac{\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right) . \frac{x^2}{2} + T_G . x}{\frac{1}{2}p . \left(\frac{\mathrm{d}T}{\mathrm{d}x}\right) . L . r\left(1 + \frac{AL}{r}\right)} . 6\mu \qquad . \qquad . \quad (5)$$

Some rough experiments have been carried out in order to see if the last equation gives values of the right order. A small ultramicroscope cell was constructed in which the top of the cell was a flat brass plate, which was also the bottom of a hollow chamber through which steam could be passed. The cell was illuminated by an arc beam, which was focused so that the edge of the beam was just touching the brass plate. Into this cell was blown tobacco smoke. The dark space was immediately observed, and with steam going through the plate, the thickness was about 0·08 cms. in the middle. Towards the edges the thickness was rather smaller, due presumably to the slightly lower temperature of the edges of the plate, which were in contact with the ebonite cell. Underneath the dark space there was a general convection current, upwards towards the hot plate, but the particles rising in the current did not penetrate into the dark space. The whole appearance was as though there was an invisible barrier, through which the gas rose but not the particles. By blowing into the cell, the dark space was momentarily destroyed, and then all the particles began to move away from the plate with a roughly uniform velocity. The time taken for the particles to move from the edge of the plate to the edge of the dark space was about 3 seconds. As the convection current upwards was of about the same order the true velocity through the gas was about twice that actually measured. Consequently the time taken to move through the dark space was about 1·5 secs.

Let us now see how this agrees with the foregoing calculations. From equation (5)

$$t = \frac{\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right) . \frac{x^2}{2} + T_G . x}{pL\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)r\left(1 + \frac{AL}{r}\right)} . 12\mu.$$

The cell was warmed by contact with the hot plate and thus the temperature of the gas T_G was on the average about 50° C. and $\dfrac{dT}{dx} = \dfrac{50}{0.08} = 625$. The average temperature in the dark space being about 75° C., the viscosity μ may be taken as 2.1×10^{-4} dynes/cm.² The particles were of about 10^{-5} cms. radius.

Consequently

$$t = 0.59 \text{ secs.}$$

We thus see, that whilst the equation gives a value of the right order, the velocity is actually about three times too great. This is probably because the value taken for $\dfrac{dT}{dx}$ is too large owing to the temperature gradient not being linear. On the whole, considering the roughness of the experiments, the agreement is satisfactory.

Whilst the above gives the explanation of why the particles move away from a hot body, it does not enable one to calculate the width of the dark space. This appears to be almost impossible because it obviously depends so much upon the convection currents, and consequently the design of the apparatus. It appears as though the temperature gradient is set up at regions very near to a hot body at a speed of the same order as molecular velocities, but that this speed, farther away from the body is much slower, being only of the same order as the ordinary convection effects and the gradient is consequently affected by them.

THE DUST-FREE SPACE SURROUNDING HOT BODIES.

By H. H. WATSON.

1. Summary.

If a hot body is placed in a chamber containing dust or smoke, and if it be illuminated suitably, a well-defined dust-free space is seen surrounding the body and extending above it as a sort of wedge. The particles in the chamber follow the convection currents set up by the hot body, but do not cross the apparent barrier of the dust-free space. The thickness of this space was found to increase as the 0.52 power of the temperature difference between hot body and ambient air, and inversely as the 0.61 power of the air pressure. The magnitude of the space is independent of the nature of the dust or of the particle size ; it depends, however, on the size and shape of the hot body, being wider the larger the body, and increasing at twice the rate for vertical plane surfaces that it does for horizontal circular rods. At atmospheric pressure the thickness of the dust-free space A is connected with θ, the temperature excess of the hot body over the ambient air, and H, the convective heat loss per unit area of the hot body per sec., by the following equation :

$$A =$$

where L is a constant, independent of the size of the body, but double the value for vertical plates that it is for horizontal rods.

A review of the various suggestions as to the cause of the dust-free space has been made. There is evidence that it is caused by a differential molecular bombardment on the particles in the very steep and varying temperature gradient near the hot body.

One practical significance of the dust-free space is discussed in a brief reference to the design of the thermal precipitator dust sampling apparatus.

2. Description of Phenomenon.

When a hot body is placed in a chamber containing dust or smoke, and illuminated suitably, it is seen that there is a well-defined dust-free layer embracing the body, and extending above it as a sort of wedge (Figs. 1 and 2). The dust or smoke particles in the chamber follow the convection currents set up by the hot body, but do not cross the apparently impenetrable barrier of the dust-free space.

Tyndall[1] and Rayleigh[2] observed only the wedge of dust-free air above the body, and Aitken[3] and Lodge and Clark,[4] working almost concurrently, were the first to observe and describe that part of the dust-free space which embraces the body.

Aitken was able to show that the effect is not due to gravitational forces, centrifugal forces, vaporisation of the particles, radiation, or electrical forces, and concluded that it is caused by the stronger molecular bombardment on the particles in a direction away from the hot body.
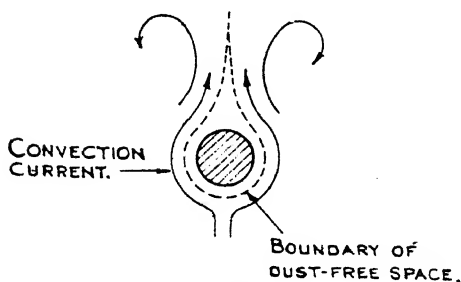

CONVECTION CURRENT.

BOUNDARY OF DUST-FREE SPACE.

FIG. I.

Lodge and Clark made a few measurements and concluded that the space increases with increasing temperature of the body, and with decreasing air pressure, and decreases with increasing molecular weight of the gas in which the phenomenon is studied.

The present investigation shows that the thickness of the dust-free space increases with increasing temperature difference between the body and ambient air (equivalent to the walls of the enclosing chamber), at a rate which is rapid at first, but begins to fall off, until at about 70° C. temperature difference it becomes sensibly constant, up to at least 250° C. difference, beyond which measurements were not made (see Fig. 5). The magnitude of the effect depends on the size and shape of the hot body, but not on the nature of that body. Horizontal circular rods and vertical plane surfaces were used in these experiments.

Although the particulate clouds used (principally magnesium oxide) were heterogeneous, with at least a 20 to 1 size range ($0·1\mu$ to $2·0\mu$ diameter), the edge of the dust-free space is sharp and well defined, indicating that, up to at least $2·0\mu$, particles of all sizes are influenced to the same degree. Similarly, the nature of the particulate cloud does not affect the thickness of the space ; such widely different substances as magnesium oxide, flint dust, carbon black, tobacco smoke and sulphur " smoke " were used.

[1] Tyndall, J., *Proc. Roy. Inst.*, 1870, **6**, 3.
[2] Rayleigh, Lord, *Proc. Roy. Soc.*, 1882, **34**, 414.
[3] Aitken, J., *Trans. R. S. E.*, 1884, **32**, 239.
[4] Lodge, O. J. and Clark, J. W., *Phil. Mag.*, 1884, **17**, 214.

The space has the same thickness round more than half of a horizontal rod and opposite most of the surface of a vertical plate, in fact, opposite all parts of a hot body not affected by the convection wedge.

There are two complications which may occur in the study of this phenomenon, both of which were observed and accounted for by Aitken. First, the apparent dust-free space may be enlarged considerably, because of the vaporisation of particles with a low boiling-point. Lenher and Taylor [5] observed this effect, caused by the evaporation of sulphuric acid mist near a hot platinum wire. The cloud produced by burning sulphur in the chamber will give two spaces for high temperatures of the body, the inner one, which is the true dust-free space, quite free from particulate matter, the outer one containing ordinary smoke, but no product of low boiling-point (*e.g.* sulphur tri-oxide) (Fig. 2). Secondly, if moisture or some other liquid is constantly evaporating from the hot surface, an enlarged space is obtained. In this respect it is interesting to note the effect when carbon tetrachloride is evaporating from a rod, which is initially at the same temperature as the surrounding air. A well-marked dust-free space is produced, but the wedge is pointing downwards, as the rod is cooled by the rapid evaporation. This observa-

tion supports the theory that the effect is due to a molecular bombard-ment. No dust-free space is produced merely by cooling the body.

3. Description of Apparatus.

The dust cham-ber, in which the experiments were made, consisted of a water-jacketed brass cylinder, A, 7·6 cm. long and 8·6 cm. internal dia-meter (Figs. 3 and 4), clamped firmly with its axis horizontal. The front end was closed by a glass window, B, while a wooden bung, D, with a central brass bush, C, was fitted into the other end.

Fig. 3

Five different bodies were used :

Body A. Vertical plane copper surface, 6·0 cm. high, 3·0 cm. wide.
Body B. Vertical plane copper surface, 3·1 cm. high, 3·0 cm. wide.
Body C. Horizontal circular copper rod, 0·90 cm. diameter.
Body D. Horizontal circular copper rod, 0·46 cm. diameter.
Body E. Horizontal nichrome wire, 0·0254 cm. diameter.

The rods passed through the bush, and were held in position along the axis of the chamber by a clamping screw. The wire was also supported along the axis, the ends passing out of the chamber through two holes in the bung. The plane surfaces were supported vertically, in the centre of the chamber and along its axis, by a bracket fixed to the bush.
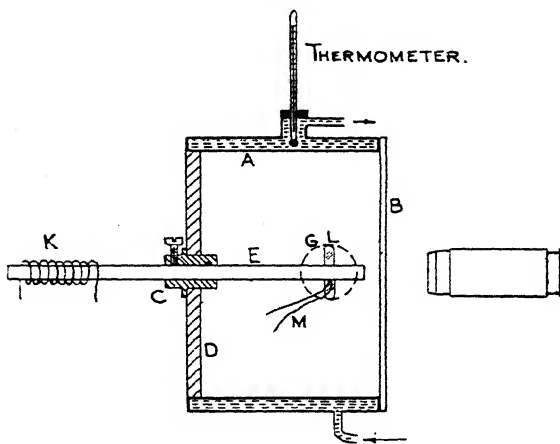
5 Lenher, S., and Taylor, G. B., *J. Amer. Chem. Soc.*, 1929, **51**, 2741.

The rods were heated electrically by a resistance coil, K, wound round the end of the rod projecting from the chamber, the heat being conducted along the rod. The wire (B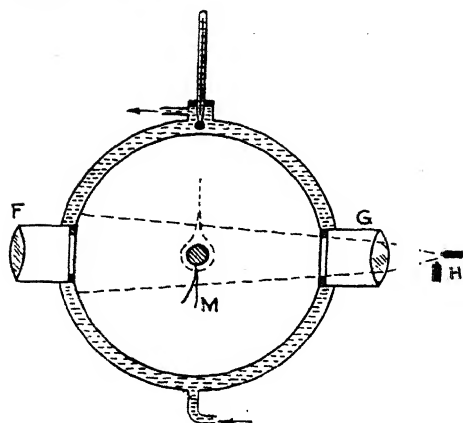ody E), was heated by an accumulator, while the two vertical planes each were made up from two similar plates with a heating coil sandwiched between them.

FIG. 4.

A small copper-constantan thermo-couple, M, was used to measure the temperatures of the rods and plates ; those of the wire were computed from its electrical resistance.

At a distance of 2·5 cm. from the front of the chamber were two windows, F, G. These were arranged at opposite ends of a horizontal diameter of the chamber, and the light from Zeiss 10 amp. automatic arcs, H, illuminated the hot body through the windows. The windows were covered by a stop, L, so that a ribbon of light, rendered only slightly divergent by a lens, entered the chamber.

TEMPERATURE DIFFERENCE BETWEEN HOT BODY & WALLS OF CONTAINING VESSEL $(\theta°C)$
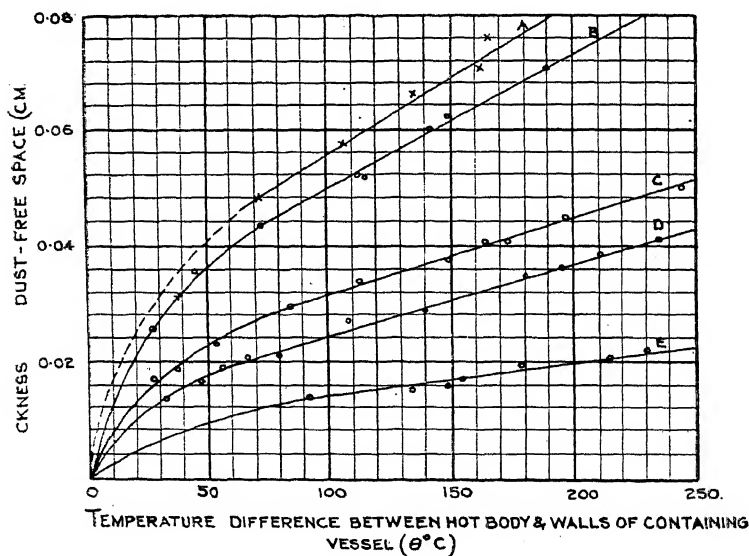
FIG. 5.

A horizontally moving travelling microscope, with its axis parallel to and on the same level as that of the chamber was used to observe and measure the dust-free space. Visibility of the space was better and measurements easier to make when dense clouds were used. Multiple scattering of light inside the chamber was reduced to a minimum by painting the walls a dull black.

The water jacket, through which tap water was running, kept the walls of the chamber at a constant measured temperature.

The thickness of the dust-free space was measured for the five bodies for temperature differences up to about 250° C.; all measurements were made horizontally outwards from the surface of the body.

4. Results.

Measurements of the thickness of the dust-free space were made, using magnesium oxide smoke, produced by burning magnesium ribbon (Table I.).

5. Accuracy of Measurements.

The thickness of the dust-free space was measured to within 0·0005 cm. The focusing of the microscope was somewhat coarse due to the large depth of focus of the optical system, and errors of about ± 3 per cent. were possible. This error would be the same for the whole of one set of observations, during which the microscope was usually not refocused. Temperatures were measured to the nearest degree Centigrade.

6. Interpretation of Results and Empirical Formulæ.

The results show that the dust-free space increases in thickness with increasing temperature difference between the hot body and the ambient air. For any one temperature it also increases with the linear dimensions of the hot body (diameter of a horizontal rod, and height of a vertical plate).

Figures for smokes and dusts other than magnesium oxide have not been reproduced, but within the experimental error of about ± 3 per

TABLE I.*

Temp. of Water Jacket. (°C.)	Temp. of Hot Body. (°C.)	Temp. Difference. θ (°C.)	Thickness of Dust-Free Space. A (cm.).
Body A. Vertical plane surface, 6·0 cm. high, 3·0 cm. wide.			
17	56	39	0·032
	88	71	0·048
	124	107	0·058
	154	137	0·066
	181	164	0·071
	184	167	0·076
	218	201	0·081
	248	231	0·092
	286	269	0·097
Body B. Vertical plane surface, 3·1 cm. high, 3·0 cm. wide.			
16	44	28	0·0275
	61	45	0·0355
	88	72	0·043
	128	112	0·052
	131	115	0·052
	158	142	0·060
	165	149	0·062
	206	190	0·0705
	261	245	0·083
Body C. Horizontal circular rod, 0·90 cm. diameter.			
10	37	27	0·017
	48	38	0·0195
	64	54	0·023
	96	86	0·0295
	122	112	0·034
	159	149	0·038
	174	164	0·0405
	182	172	0·041
	206	196	0·0445
	254	244	0·0495
Body D. Horizontal circular rod, 0·46 cm. diameter.			
10	42	32	0·0135
	57	47	0·0165
	66	56	0·019
	76	66	0·0205
	90	80	0·0215
	118	108	0·027
	150	140	0·029
	190	180	0·0345
	205	195	0·036
	221	211	0·0385
	245	235	0·041
Body E. Horizontal wire, 0·0254 cm. diameter.			
10	92	82	0·0135
	143	133	0·015
	158	148	0·016
	164	154	0·017
	187	177	0·0195
	223	213	0·0205
	240	230	0·022

* These results are plotted in Fig. 5.

cent. they agree with those for magnesium oxide.   The figures of Table I.
were plotted on logarithmic scales and the following general relation
between A and θ obtained :—

$$ \qquad \qquad \cdot \qquad \cdot \qquad \cdot \qquad \cdot \quad \cdot \quad \cdot \quad (\text{1}) $$

where A is the thickness of the dust-free space, θ is the temperature
difference, K and α are constants.

The values of K and α for the different bodies are given in Table II.

Miyake[6] has made recently some measurements of the dust-free
space surrounding vertical platinum ribbons, 3 to 10 cm. long and 0·5 cm.
wide. He found that the thickness
of the space increased as the 0·7
power of the temperature difference.

To obtain a single formula for all
bodies, the way in which K varied
with the shape and size of the body
was studied.   The rate of convective
heat loss from a hot body is given
by :—

$$ H = C\theta^{1\cdot25} \qquad . \qquad . \quad (2) $$

where H is the convective heat loss
per sec. from unit area of the hot
surface, and C is a constant which

TABLE II.

Body.	Value of K.	Value of α.
A	0·0061	0·51
B	0·0054	0·55
C	0·0035	0·49
D	0·0027	0·55
E	0·0015	0·52

Mean value of α = 0·52

varies with the shape, size and orientation of the body.   The value of
C has been determined experimentally for horizontal rods and vertical
planes.   It is independent of the length of rod and width of vertical
plane, and its values for the five bodies have been obtained from curves
given by Fishenden and Saunders,[7] and are tabulated in Table III.,
θ being given in ° C. and H in calories per sq. cm. per sec.

TABLE III.

Body.	Value of C of Equation (2).
A	$1\cdot03 \times 10^{-4}$
B	$1\cdot53 \times 10^{-4}$
C	$0\cdot93 \times 10^{-4}$
D	$1\cdot25 \times 10^{-4}$
E	$5\cdot87 \times 10^{-4}$

TABLE IV.

Body.	Value of L.
A	$15\cdot2 \times 10^{-5}$
B	$15\cdot9 \times 10^{-5}$
C	$8\cdot2 \times 10^{-5}$
D	$7\cdot1 \times 10^{-5}$
E	$7\cdot4 \times 10^{-5}$

The best relationship between C and K is :-

$$ \qquad \qquad \qquad \cdot \quad (3) $$

where L is a constant.

The equations now reduce to :—

$$ A = L\theta H^{-0\cdot38} \qquad\qquad (4) $$

Values of L, obtained by substituting the actual recorded values of
A and θ, and the calculated values of H in equation (4) are given in
Table IV.

[6] Miyake, S., *Report of the Aeronautical Research Institute, Tokyo University,*
1935, **10**, 85.
[7] Fishenden, M., and Saunders, O. A., *Calculations of Heat Transmission,* p. 103
(London, H.M.S.O., 1932).

The mean value of L for vertical planes is thus $15\cdot6 \times 10^{-5}$, and for horizontal rods $7\cdot6 \times 10^{-5}$. It is interesting to note that L is almost double the value for vertical planes that it is for horizontal rods. We may obtain, therefore, the thickness of the dust-free space for horizontal rods and vertical planes of any size from equations (5) and (6).

Horizontal rods :—

$$A = 7\cdot6 \times 10^{-5}\,\theta H^{-0\cdot38} \qquad . \qquad . \qquad . \quad (5)$$

Vertical plane surfaces :—

$$A = 15\cdot6 \times 10^{-5}\,\theta H^{-0\cdot38} \qquad . \qquad . \qquad . \quad (6)$$

where A is in cm., θ in degrees Centigrade, and H in calories per sq. cm. per sec.

7. Effect of Air Pressure on the Dust-Free Space.

W. G. Iles has extended this work and has investigated the effect of air pressures less than atmospheric on the thickness of the dust-free space. He used an electrically-heated vertical plane surface $3\cdot1$ cm. high (Body B), and made measurements at five different temperatures, determining the thickness of the space at various pressures for each temperature of the body. He found that, at any one temperature, the thickness of the dust-free space opposite the plane vertical surface, $3\cdot1$ cm. high, varied inversely as the $0\cdot61$ power of the pressure, P. His results are summarised briefly in Table V.

For the plane vertical surface, therefore, we may combine the variation of A with θ and P in the one equation :—

$$A = B^1 \qquad . \quad (7)$$

TABLE V.

Temp. Difference θ (°C.).	Value of C in Formula $A = BP^{-C}$.
41	0·61
68	0·63
88	0·59
145	0·58
181	0·61

Mean value of C : 0·61

The relation between thickness of dust-free space and air pressure, calculated from the figures given by Lodge and Clark (*loc. cit.*,[4] p. 226) for a horizontal rod of carbon give :—

$$A \alpha P^{-0\cdot65}$$

It appears therefore that the pressure effect and formula (7) is the same for all bodies, although this will have to be verified by further experiments, especially as Miyake,[6] found for a vertical platinum ribbon that :—

8. Review of Suggested Explanations of Phenomenon.

The idea of a simple differential molecular bombardment on the particles to produce the dust-free space does not explain why the edge of the space is fixed and well defined. It can be proved that, due to the differential molecular bombardment in a temperature gradient, there should be a force on a small particle, which is directly proportional to the temperature gradient dT/dx. A temperature gradient exists at every point between the hot body and the walls of the experimental chamber, but the dust-free space does not grow to fill the chamber. There must be some retarding action which stops the effect at a small distance, A, from the hot body. It seems possible that, in the rapidly moving convection stream, the effect of the thermal force does not have time to develop beyond a certain distance.

Very near to a hot surface (within 0·1 cm.) the temperature gradient is very large, although the precise way in which the temperature varies within this distance is not known. In this connection Randas and Malurkar [8] are hoping to explore the first 0·1 cm. from a hot surface. It seems probable, therefore, that there is a definite minimum value of dT/dx required to produce the effect, the force due to which is just balanced at the edge of the dust-free space by some force which is connected with the rate of the convection stream, and hence the loss of heat due to convection, H. We may write in a general way :—

$$F(dT/dx) = H \qquad . \qquad . \qquad . \qquad . \qquad (8)$$

The temperature gradient at any point will depend on the temperature difference, θ, between the hot body and the ambient air, and inversely as some function of the distance from the hot body. At the edge of the dust-free space, at a distance A from the hot body, we have therefore :—

$$F\left(\frac{1}{A}, \theta\right) = H \ . \qquad . \qquad . \qquad . \qquad (9)$$

Equation (9) is of the same form as the empirical equation (4).

Bancroft [9] has suggested that if a particle is heated on one side, the film of adsorbed air on that side will be diminished in thickness, with the result that air will flow round the particle from the cooler to the warmer side, tending to restore equilibrium. The result will be that the particle is sucked away from the hot body. Bancroft considers that this action and that due to a molecular bombardment take place simultaneously. It is unlikely, however, that the film of adsorbed air will be of the same thickness, or held with the same force, by such widely different substances as carbon and magnesium oxide, but the thickness of the dust-free space is the same to within about 5 per cent.

That radiation has no influence in producing the dust-free space is evident from one or two simple experiments. Aitken, for instance, observed that the space was of the same thickness opposite both halves of a hot plate, one half highly polished and the other half blackened.

In a recent paper, Miyake [6] has suggested that the dust-free space is due to the Magnus effect, produced as the result of the velocity gradient near a hot body. At the surface of a hot body there is no air movement, but the upward velocity of the convection current increases with the distance from the surface until, at a small distance away, it reaches a maximum, and afterwards decreases, but at a slower rate. Miyake found this distance of maximum velocity to be about twice the distance of the edge of the dust-free space from hot vertical platinum ribbons. A particle within the dust-free space will be always nearer the hot body than this region of maximum velocity. It will thus have a slightly smaller velocity of air movement, due to the convection stream, past the side nearest the hot body than past the side more remote. This will produce a spin, and the consequent drag on the particle in the moving air stream, or Magnus effect, will move it away from the hot body.

Now, a velocity distribution, zero at the surface and increasing to attain a maximum value at a short distance from the surface, such as that due to convection currents past a hot body, exists when air is flowing past a surface, whether that surface is warmer, cooler or at the same temperature as the dusty air. In each of these cases, the theory would

[8] Randas and Malurkar, *Ind. J. Physics,* **6**, part 1 ; **7**, part 6.
[9] Bancroft, W. D., *J. Physic. Chem.*, 1920, **24**, 421.

demand the Magnus effect to produce a drift away from the body. No dust-free space is observed, however, opposite a body which is colder than or at the same temperature as the air streaming past it ; it is only formed round a hot body. The Magnus effect, therefore, does not produce a dust-free space.

It seems fairly certain that the phenomenon is produced by a differential molecular bombardment, and for this to be effective the value of dT/dx must be above a certain minimum ; this minimum depending on the temperature difference between hot body and ambient air and the rate of convective heat loss.

9. Thermal Precipitator Dust Sampling Apparatus.

Consider a wire, W, (seen in section in Fig. 6) placed in a horizontal position centrally between the two opposite plane surfaces, A and B, of a narrow vertical channel ; suppose that the wire is heated to a temperature at which the thickness of the dust-free space in free air is at least as large as the distance between the wire and either plane surface. Then, if air containing dust or smoke is drawn down towards the wire the particles will not be able to penetrate the dust-free barrier extending across the channel. The particles will be deposited just above b and b^1, where the dust-free space comes into contact with the surfaces. The air, freed from particles, will pass by the wire.

This, briefly, is the principle on which the thermal precipitator dust sampling apparatus [10] has been constructed. A wire similar to body E, 0·0254 cm. diameter, is used and

BOUNDARY OF
DUST-FREE SPACE

FIG. 6.

the deposit of dust or smoke is obtained on cover-glasses arranged just within the dust-free space. The dust record can be examined microscopically.

This dust sampling instrument is practically 100 per cent. efficient, a feature which makes it very suitable both in the laboratory and in factories and mines for estimating accurately the dust or smoke concentration.

My thanks are due to Mr. J. D. Fry, who suggested this investigation, for his continued interest and advice.

[10] Green, H. L., and Watson, H. H., *Medical Research Council*, Special Report Series, No. 199 (H.M.S.O., 1935).

GENERAL DISCUSSION.*

Mr. C. H. Bosanquet (*Billingham*) said : At high pressures with large connecting tubes between the bulbs the Knudsen thermal pressure difference effect breaks down, not through convection, but owing to the return flow due to gas pressure. The initial rate of thermal transpiration is proportional to the temperature gradient and the cross-section of the tube. The return flow is proportional to the pressure gradient, and the square of the cross section. Unless the capillary is very small, the full Knudsen pressure difference cannot then be approached.

The number of molecules approaching the hot plate must be equal to the number leaving it in the same time, but their mean velocity is less,

* On two previous papers.

giving a transport of momentum away from the plate, and driving away the particles in a manner analogous to the action of a Crookes' radiometer. This should show up as a force on the plate, though a search tube would not necessarily show a pressure, since the temperature gradient at its mouth would be less than that at the surface of the plate.

Dr. T. L. Ibbs (*Birmingham*) said : The work of both authors leads to the conclusion that the dust-free space round a hot body is directly associated with the temperature gradient. This effect is similar to the thermal diffusion effect [1] in gases ; simple experiments we have made from time to time on smokes appear to confirm the influence of the temperature gradient on the separating effect.

Chapman [2] has considered the question of brownian displacements and thermal diffusion of grains suspended in a fluid, and predicted a separating effect. In a smoke suspension there are therefore all the conditions required for a thermal separating effect ; and the dust sampling apparatus described by Watson shows the practical efficiency of a temperature gradient as a separating device. Tentative calculations made by Dr. B. E. Atkins support the idea that the separation produced by a small temperature difference might be considerable. The question raised by Sir Robert Robertson as to the cause of the black marks on walls near radiators and steam pipes appears to be explained by the tendency of dust particles to move down a temperature gradient, causing them to be deposited on a cold surface.

The apparatus used in many experiments on this subject has taken the form of a hot wire in a large enclosure, and the dust-free space has been observed near the wire. The conditions are complex, as there will be a layer of gas practically at rest near the hot wire, surrounded by gas in considerable movement due to convection. This limits, in effect, the extent of the temperature gradient, and consequently the thermal separation, to a small region round the wire. The increase in the width of the dust-free space obtained by reducing the air pressure is probably due to the reduced effect of convection, with a consequent extension of the temperature gradient. To obtain further progress, convection should be avoided as far as possible.

Professor K. G. Emeleus (*Belfast*) said : Useful information about the distribution of density in the gas near the hot body—and hence its temperature—also about the possible presence of local eddies in the convective streaming, would probably be obtained by using an interferometer.

Mr. A. G. Grant (*Darlington*) said : Prof. Whytlaw-Gray suggested in his introductory paper that the thermal precipitation phenomena might have a practical application to the industrial removal of dispersoids from gases. From the present discussion it seems evident that the dust-free zone breaks down for gas velocities much above zero. From this, it seems as though the phenomena cannot in fact find an industrial application ; this being the case, will the authors explain what, apart from the evolution of the thermal precipitator for obtaining dust slides, is the object and value of this work ?

Professor R. Whytlaw-Gray (*Leeds*), in reply, said : My reference in the introductory paper was not meant to suggest that thermal precipitation has at present any industrial applications. It is, however, of interest as it involves an effect which has hardly been studied and the explanation of which is still somewhat obscure. A closely related phenomenon is the deposition of particulate matter on cold surfaces from hot disperse systems. This too needs investigation.

[1] See references in *Proc. Physic. Soc.*, 1931, **43**, 142 ; see also T. L. Ibbs and A. C. R. Wakeman, *Proc. Roy. Soc.*, A, 1932, **134**, 613 ; P. H. Emmett and J. F. Schultz, *J. Amer. Chem. Soc.*, 1932, **54**, 378 ; 1933, **55**, 1376 ; and 1933, **55**, 1930 ; G. and O. Bluh, *Z. Physik.*, 1934, **90**, 12.

[2] S. Chapman, *Proc. Roy. Soc.*, A, 1928, **119**, 34 ; and *Proc. Roy. Soc.*, A, 1928, **119**, 55.

Mr. T. C. Angus (*London*) said : Should the downward air velocity in the thermal precipitator be not substantially greater than the natural upward velocity due to the convection currents from the hot wire ?

Dr. R. Meldau (*Berlin*) said : If a hollow metal sphere of about 10 cm. diameter and pierced with fine holes is used as a condenser in a high tension field of 30,000 to 40,000 volts, and a fog or vapour cloud is forced through the holes, the fine particles take up to a very large extent a unipolar charge. Such an arrangement has been utilised by the firm Koerting of Hannover for inhalation apparatus and Dr. Wedekind, Cologne, reported upon experiments with it in the *Zeitschrift für Balneologie*, Sprüng, 1936, giving remarkable results.

Mr. C. F. Goodeve (*London*) (*communicated*) : I think that a quantitative treatment of the dust-free space cannot satisfactorily be made until the experimental arrangement is such that convection is avoided completely and controlled temperature gradients are obtained. The fact that the dust-free space has the same thickness at points around most of the horizontal rod seems an unexpected coincidence. Apparently, the variation in velocity of the convection current exactly compensates the variation in thickness to be expected from the different times the particles are in the temperature gradient.

Bancroft's suggestions, referred to in this paper, that smoke particles are " sucked " in a temperature gradient cannot of course be taken seriously.

Dr. W. Cawood (*Leeds*), in reply, said : In answering criticisms regarding the small cylinders of radius of the order of the mean free path in which Knudsen's Laws (*i.e.*, $N_1 c_1 = N_2 c_2$) hold, I would like to point out that this is the fundamental assumption of the attempted explanation of the phenomena. Unless something of this kind is postulated one would expect a force even on objects of a much greater size, such as small vanes, etc. As far as I know, such forces are not obtained.

I will explain the idea of these small cylinders a little more fully. Imagine a cylinder about 1 mm. wide moving with a convection current. Then, considering only the movements of the molecules parallel to the axis of the cylinder, there will be mass movements of the gas in the cylinder, because the velocity at one side will be greater than at the other. As the radius gets smaller the difference of velocity will get less and it seems quite reasonable to suppose that in a cylinder of which the radius is of the order of the mean free path, there will be no difference of velocity and the cylinder of gas will move bodily in the convection current without mass movements inside it.

Mr. H. H. Watson (*Porton*), in reply, said : Sir Robert Robertson has referred to the deposition of dust on walls and the pattern staining on ceilings. Particles of smoke and dust in the air of a room are carried upwards by convection currents and are blown about in all directions by draughts. When these particles, often in quite rapid motion, are brought into contact with the walls, ceiling and furniture of the room they are deposited there, if the solid surface is cooler than the surrounding air.

For instance, there is usually a black deposit on the wall just above a hot water " radiator " or pipe. The convection currents bring many more particles into contact with the wall than does normal diffusion, and the conditions are right for deposition there. It is perhaps not so much due to a thermal force causing the particles to move down the temperature gradient on to the cool surface of the wall, as to the fact that the wall is not protected by a dust-free space.

The replica in light and shade on a ceiling of the construction in, and immediately behind, the plaster is a familiar sight, especially in industrial towns. When there is a wooden lath backing to the plaster, that part of the ceiling not backed by the laths is cooled by the air circulating above the ceiling, and dust can be deposited there. The laths insulate the remainder of the ceiling very efficiently, and dust cannot be deposited if the surface temperature is above that of the ascending air, because of the

protecting dust-free space. When the ceiling is backed by steel girders, as in the Chemistry Department of the University of Leeds, we have an inverse effect. That part of the ceiling backed by the girders is kept comparatively cool and a deposit is obtained there. To prevent pattern staining the temperature of the ceiling must be uniform over its surface. Work to attain this end has been done by Bonnell and Burridge.[3]

In rooms heated by direct radiation, as by an open fire, the walls and furniture are warmer than the air. They are thus protected by a dust-free space, and the dust in the air tends to remain in suspension, and is not deposited to the same extent as when the air is heated by convection, *i.e.*, by steam pipes or hot water "radiators," for then the air is usually warmer than the walls and furniture, and there is no protecting dust-free space.

In reply to Mr. Angus : If a thermal precipitator is supported alone in a dusty atmosphere, without a water aspirator or a source of suction, the convection stream from the wire pulls air upwards through the instrument at a rate which is so small that a very sparse dust deposit is obtained. This shows that the suction velocity is large compared with the opposing convection velocity.

In reply to Dr. Ibbs and Mr. Goodeve : I agree that much useful information would be obtained by studying the dust-free space when convection has been eliminated. We also want precise information about the variation of temperature within the first millimetre from a hot surface. For the practical application of the phenomenon, however, the space must be examined as it occurs in free air, and the empirical formulæ 5 and 6, which I have obtained, used.

[3] D.S.I.R., *Building Research Bulletin*, No. 10 (H.M.S.O., 1931).

THE DETERMINATION OF SIZE DISTRIBUTION IN SMOKES.

By H. S. PATTERSON and W. CAWOOD.

Smokes, unless dispersed under very special conditions which we have previously described,[1] consist of particles varying very considerably in size. The determination of the size frequency or size distribution, that is, the numbers of particles of different sizes present, is a matter of considerable difficulty. Generally speaking, the methods which have been attempted fall into three categories, firstly, those in which a simultaneous measurement is made of a number of particles suspended in air, secondly those in which some property of the particles is utilised to obtain separation of the various sizes, which can then be enumerated, and lastly those in which the smoke is allowed to sediment and an estimate of the size frequency.

The first method is necessarily photographic, since it is impossible visually to estimate simultaneously a number of particles, and if they are measured successively, they tend to be selected rather than chosen at random. An ingenious photographic attempt was made by Wells and Gerke [2] who photographed the traces as seen in an ultramicroscope,

[1] *Proc. Roy. Soc.*, 1932, **136A**, 538.
[2] *J. Amer. Chem. Soc.*, 1919, **41**, 318.

in a stream of charged particles moving horizontally under photophoresis in a vertical alternating electric field. Each particle traverses a zig-zag path, by measurement of which its size can be deduced if its effective density and electric charge are known. Since there is considerable doubt as to both of these quantities the method cannot be used to give an accurate size distribution.

This method has been developed and improved by Fuchs and Petrianow [3] who apply an alternating potential at right angles to the particles falling under gravity.

From the zigzag traces obtained photographically, both the charge and mass can be calculated and from the tracks of a large number of particles the size distribution can be obtained ; this method can be used for particles of radius of $0\cdot3\mu$ but for smaller particles it is untrustworthy. Whilst for droplets this method is reliable, for aggregates such as are usually present in smokes, the evaluation of the effective density is difficult and hence the calculation of the radius from the mass is uncertain.

For coarse smokes we have attempted to photograph the vertical traces due to particles falling in the field of the ultramicroscope, but our results appeared to be of little value owing to the difficulty of avoiding convection currents.

The second method has been used by Rohmann [4] who charged a narrow ribbon of particles by passing it through an ion stream and then precipitated the particles on to paper by means of an electric field. Under these conditions the charge caught by the particles is probably proportional to the square of their radius and hence on deposition separation of the various sizes should occur. This method has given good results with dust, but is unsatisfactory for the finer disperse systems. Regener,[5] on the other hand, has suggested passing a smoke at varying velocities through a spiral, when particles above a certain size should be removed by centrifugal action, and counting the residue. In this case, the results would probably be vitiated owing to increase in the velocity of coagulation.

For particulate systems consisting of solid nonhygroscopic particles, sedimentation on to a slide, followed by microscopic measurement has frequently been used, and various types of sedimentation boxes in which a column of the smoke or dust is allowed to settle on to a microscope slide or cover glass, have been devised. The deposit is examined microscopically by transmitted light using an objective of high resolving power, and the particles are measured by an eyepiece micrometer. This method is both slow and laborious and, moreover, can only be applied to particles which are well within the limit of resolution of the microscope.

To overcome these difficulties we have carried out investigations along two lines.

(1) Photometric Method.

In this method, the deposit which in our experiments we obtained in a collector slide by means of the apparatus already described * was illuminated from the front to give a dark field as for counting. It was

[3] *Koll. Z.*, 1933, **65**, 171.   [4] *Z. Physik*, 1923, **17**, 253.
[5] Freundlich, *Colloid and Capillary Chemistry*, 1922, 774.
* See page 1056.

then observed with a special eyepiece previously described [6] containing an artificial particle. The brightness of the artificial particle could be varied by means of a neutral wedge and matched in brightness against individual particles in the deposit. In this way, if the law of scattering is known it is clearly possible to deduce the relative sizes of the particles, and divide up the total number into groups according to size. In practice the method proved somewhat laborious, but it is the only way available at the present time for investigating small particles. The most serious objection, however, is that the law of scattering varies considerably for particles having a radius in the neighbourhood of 10^{-5} cm., the index diminishing for homogeneous particles from the sixth power to the square of the radius with a comparatively small increase in size. For coarse smokes with particles well above this limit, the method should, however, be able to be applied easily. A typical coarse smoke is that obtained by burning magnesium ribbon and measurements have been made with this material. The law of scattering in this case has been previously measured over a fairly long size range [1] for particles suspended in the air, but since this smoke consists of loose complexes which on settling tend to flatten somewhat a further complication is introduced. The results obtained, though incapable of precise interpretation, showed clearly the progressive variation of size frequency as coagulation proceeded.

(2) Graticule Method.

By the examination of smoke deposits by direct light under the microscope using a high resolving optical system, it has been found possible, with the help of a specially designed graticule, to estimate rapidly the size frequency of particles ranging from about $1 \cdot 10^{-5}$ to $25 \cdot 10^{-5}$ cm. radius. A suitable deposit can be obtained in the very early stages of a smoke by using a collector slide holder * 2 mm. deep, and in the later stages 5 or 10 mm. deep, according to the number of particles. In practice for the graticule used a collector slide holder about 1 cm. deep gives a convenient density of deposit for a smoke containing about a quarter million particles per c.c. Instead of collecting the deposit in the usual way, the bottom collector slide is replaced by a brass plate carrying a No. 1 microscope cover glass. The brass plate in the collector slide holder is pulled in the ordinary way and after allowing time for sedimentation, the cover glass is removed and carefully mounted on a thin glass microscope slide. The optical systems which we have found best for obtaining the clearly defined images essential for satisfactory results consists of a 2 mm. apochromatic objective N.A. 1·40, used with a ($\times$ 12) compensating ocular and a substage achromatic condenser of aplanatic aperture as near N.A. 1·0 as possible. There is no gain in using an oil immersion condenser, since the deposit is mounted dry. This combination gives a $\frac{2}{3}$ cone in the objective, which

Fig. 1.

6 Patterson and Whytlaw-Gray, *Proc. Roy. Soc.*, 1926, 113A,
* See p. 1056.

is often considered to be the best working condition. As illuminant we have used a pointolite lamp together with a green or blue light filter.

The graticule, which is inserted in the focal plane of a ($\times$ 12) compensating eyepiece, consists of a rectangle and a series of ten numbered circles and corresponding discs as shown enlarged in Fig. 1. These appear superimposed on the deposit as seen in the field of the microscope. The images of the circles and discs correspond in size to particles ranging from $1 \cdot 10^{-5}$ to $25 \cdot 10^{-5}$ cm. radius when the deposit is viewed with a 2 mm. Leitz apochromatic objective N.A. $1 \cdot 40$ and a tube length of 17 cm. The size of the rectangle under these conditions is $5 \cdot 10^{-3}$ by $2 \cdot 22 \cdot 10^{-3}$ cm. and for a different optical system the graticule can be standardised by measuring the dimensions of the rectangle with a stage micrometer. These graticules have been made to our design by Messrs. Rheinberg. The particles contained within the rectangle can be rapidly matched by eye against the discs or circles and their sizes determined. Since as a rule there are only about 6 particles in the rectangle, it is necessary to match a large number of fields, usually about 50, in order to obtain a good average. The numbers of the various sizes are noted down and a record is kept of the number of rectangles estimated. Since the area of the deposit corresponding to the rectangle and the depth of the collector slide holder are known, the number of particles per c.c. of the different sizes is easily calculated. The sum of the numbers per c.c. of all the sizes, gives, of course, the total number of particles per c.c. of the smoke. With a little experience the size
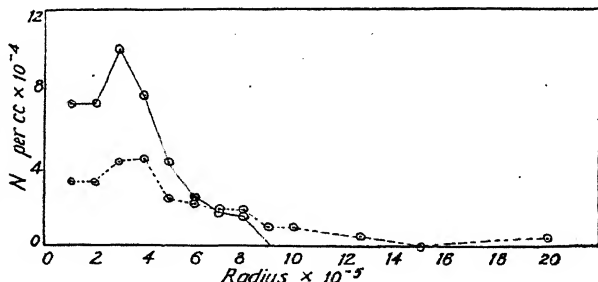
FIG. 2.

distribution may be estimated by this method both rapidly and accurately. If as a check a circle is occasionally superimposed on a particle by moving the mechanical stage, it will be found that the estimate of size is practically never in error. It may be noted that whilst with a coarse smoke all the particles will be seen and enumerated by this method, with a fine smoke the smallest particles are likely to be invisible and in this latter case the total number should be counted by the special ultra-microscope cell or the collector slide method.[6] Actually, of course, the limit of visibility of small particles viewed by transmitted light, lies well below the limit of resolution. On this account, the smallest particles will all be reckoned as being of radius $1 \cdot 10^{-5}$ cm., whilst some of them may be below this size. It may be noted that the method can only be applied to non-hygroscopic particles of fairly high melting-point. It is not suitable for example for stearic acid, since the particles of this material tend to melt and spread due to the heat focussed by the condenser. Again, with loose aggregates such as the particles of magnesium oxide, an error may be introduced due to some flattening occurring on settlement. For the investigation of spherical particles such as those formed by the dispersion of certain dyestuffs or of fine dusts such as silica, the method is, however, reliable.[7]

Some results obtained with magnesium oxide smoke dispersed by

[7] *Cp.* Green and Watson, *Medical Research Council Report,* No. 199.

burning 6 ins. of ribbon in a cubic metre chamber are shown diagrammatically in Fig. 2.   The more rapid disappearance with time of the smaller particles is evident.   In this case only two deposits taken at 10 and 32 minutes from the start were counted.

The further application of this method should afford a means of tracing the change in size distribution during the life history of disperse systems in gases, provided the minimum size of particle is greater than 0.2μ radius.

THE COHESION BETWEEN SMOKE PARTICLES.

By R. Stevenson Bradley.

The assumption is usually made that smoke particles will stick together on collision.   With a liquid dispersion medium there is evidence [1] that this is not always true, and that a reverse may proceed at the same time as a direct coagulation.   With smoke particles, however, reflexion after collision has not been observed, but a pair of particles often gyrate round their centre of gravity at what appears to be a slight distance apart.   It is of interest, therefore, to study the conditions of temperature, size of particle, surface energy, etc., under which cohesion occurs with solid particles.   In the case of liquid particles the lower energy consequent upon the formation of a large drop, due to decreased surface, will usually ensure coalescence, although the reverse occurs when a living cell breaks up into two units.

The cohesion between solid spheres has been derived theoretically by the writer,[2] and studied experimentally with quartz spheres.   If we assume a very general law of force f between molecular centres,[3] the cohesive force of attraction between two spheres of radii r_1 and r_2 is very nearly

$$F = 4\pi^2 q^2 \frac{r_1 r_2}{r_1 + r_2}\left[\frac{\lambda}{(n-1)(n-3)(n-4)(n-5)d^{n-5}} - \frac{\mu}{(m-1)(m-3)(m-4)(m-5)d^{m-5}}\right],$$

where $f = \frac{\lambda}{r^n} - \frac{\mu}{r^m}$, q is the number of molecules per c.c. and d the smallest distance between the centres of the surface molecules of the two spheres.   Flattening of the spheres is not considered.   The same assumptions, neglecting such refined considerations as the energy involved in the rearrangement of the surface molecules on the formation of a new surface, give for the surface energy of the solid [4]

$$\sigma = \pi q^2\left[\frac{\lambda}{(n-1)(n-3)(n-4)(n-5)d^{n-5}} - \frac{\mu}{(m-1)(m-3)(m-4)(m-5)d^{m-5}}\right].$$

Hence
$$F = 4\pi\frac{r_1 r_2}{r_1 + r_2} \cdot \sigma \qquad . \qquad . \qquad . \qquad . \quad (1)$$

[1] Colloid Symposium Monograph, 1925, **2**, 68.
[2] Bradley, *Phil. Mag.*, 1932, **13**, 853.
[3] Lennard-Jones, *Proc. Physic. Soc.*, 1931, **43**, 461.
[4] Bradley, *Phil. Mag.*, 1931, **11**, 846.

The same value of d will appear in the expressions for F and σ if the surface molecules of the spheres are in contact at the point of contact. Equation 1 was subsequently derived by another method by Derjaguin.[5]

In practice it was found that F varied linearly with $r_1 r_2/(r_1 + r_2)$ in the case of spheres of quartz and sodium borate.

These conceptions may be applied to the cohesion of smoke particles, since equation 1 is independent of the precise form of the law of force. The most obvious force tending to cause reversal of coagulation is the Brownian motion. Considering first the rotation, for a double particle formed from two spheres of radii r_1 and r_2, we have $\frac{1}{2}I\omega^2 = kT$, where ω, k and T are the angular velocity, gas constant and absolute temperature, assuming that the double particle has the mean energy of rotation for the temperature concerned. If the density is ρ, $I = \frac{2}{15}\pi\rho(r_1^5 + r_2^5)$. The centrifugal force tending to cause disruption is

$$\tfrac{4}{3}\pi\rho\omega^2(r_1^4 + r_2^4) = \tfrac{4}{3}\pi\rho\tfrac{15}{14} \cdot \frac{kT(r_1^4 + r_2^4)}{\pi\rho(r_1^5 + r_2^5)}.$$

Hence the point at which centrifugal overcomes cohesive force is given by

$$\tfrac{10}{7}kT\frac{r_1^4 + r_2^4}{r_1^5 + r_2^5} = 4\pi\frac{r_1 r_2}{r_1 + r_2}\sigma \qquad . \qquad . \qquad . \quad (2)$$

This result is independent of the flattening which may occur on cohesion ; the deformation differs markedly from that considered by Hertz for the case of two spheres pressed together, for then the pressure acts throughout the mass, whereas with cohesion only neighbouring layers of molecules are attracted towards one another. At the point at which centrifugal force overcomes cohesion the spheres are just about to part company, and there is no flattening, so that the above results are strictly true.

When $r_1 = r_2 = r$, equation 2 gives $r = \left(\dfrac{5}{7}\dfrac{kT}{\pi\sigma}\right)^{\frac{1}{3}}$. The cases of interest are approximately isomorphous solids, since with crystalline particles departure from the spherical shape will be serious. We should expect quite a low value of σ, about 30 dynes per cm. This gives for r a value of approximately 10^{-8} cm., i.e. all smoke particles of equal size will cohere. Even at $3000°$ r is only 5×10^{-8} cm. Hence the fact that equipartition is actually replaced by a Maxwellian distribution hardly affects the argument, since an infinitesimal fraction of particles will have sufficient energy of activation at room temperature. Disruption due to collisions will give similar results.

With particles of different sizes similar remarks apply. If $r_1 \gg r_2$ equation 2 becomes $\dfrac{10}{7}\dfrac{kT}{r_1} = 4\pi r_2\sigma$. Hence $r_1 r_2 = 2 \times 10^{-16}$ at room temperature. A very small particle will cohere with a large one even if it will not do so with one of its own size.

Chains and aggregates of particles give similar results, e.g. with a linear chain of four particles breaking in the middle it can be shown that $r^2 = \dfrac{5}{54}\dfrac{kT}{\pi\sigma}$, which gives values of r smaller than before.

Although impossibly high temperatures would be necessary to obtain disruption with particles of the size usual in smokes, the velocities of the particles required is small compared with molecular velocities at room

[5] Derjaguin, *Kolloid. Z.*, 1934, **69**, 155.

temperature, and the requisite velocity can be reached by violent fanning of the cloud, which sets up eddies, so that particles acquire relative velocity. A particle of density 2 travelling at 30 miles per hour will have sufficient kinetic energy to disrupt a stationary doublet of two particles each of radius 10^{-6} cm. if its radius is approximately 4×10^{-4} cm. With greater velocities (v) the radius of the heavy particle will be increased according to $v^{\frac{2}{3}}$; at 30 miles per hour a doublet of particles of radius 10^{-5} cm. requires a heavy particle of radius approximately 10^{-3} cm. for disruption. Cohesion in a large aggregate is confined to the separate cohesions between the component particles, and if one of these on the outside of a large complex were hit by another large complex with sufficient relative velocity disruption could occur. The medium may also impart rotational energy to complex particles, causing disruption. Hence for a violently fanned cloud the normal coagulation might be replaced by an approximately stationary state, owing to a rough balance between coagulation and disruption. Unpublished work of Dr. Colvin and the author working under the direction of Professor Whytlaw Gray showed that stationary states could be produced by violent fanning.

Coagulation in smoke proceeds partly because of the size of the particles. In actual practice the particles will be covered with a layer of adsorbed gas, but it is probable that the solids break through this at the point of contact. If this is not so, then the cohesion between the solids is still given by the same formula, but the distance d becomes d_1 and is no longer equal to the molecular diameter. Hence

$$F = 4\pi\frac{r_1 r_2}{r_1 + r_2}\sigma\left(\frac{d}{d_1}\right)^{m-5}$$

approximately, neglecting the repulsive term. To this must be added a term representing the cohesion of the two adsorbed layers. The latter may represent a repulsion if the adsorbed layers have, *e.g.* dipoles oriented perpendicular to the surface. A thin film of water could reduce the cohesion very considerably. When the coagulated particles are immersed in water they may be peptised, owing to the growth of the adsorbed layer. Wo. Ostwald and Haller [6] have shown that the volume assumed by many colloidal precipitates is dependent on the dispersion medium, the thickness of the layer round a particle being about 1μ, and this effect is correlated with the dipole moment of the dispersion medium.

When the smoke particles are crystalline approximate calculations may be made. With two cubic particles of edge r face to face the cohesive force is approximately

$$F = \frac{\pi q^2 \mu r^2}{(m-1)(m-3)(m-4)d^{m-4}}.$$

Hence $F = \frac{\sigma}{d}r^2(m-5)$. This gives results similar to those obtained with spheres.

[6] Wo. Ostwald and Haller, *Kolloid Beih.*, 1929, **29**, 354.

THE SIZE-FREQUENCY OF PARTICLES IN MINERAL DUSTS.

By H. L. GREEN.

Dusts, in the colloid sense, may be classified as disintegration aerosols, and are formed by the release into the air of particles produced by the disintegration or disruption of solid matter. The term " dust cloud " is frequently used to distinguish the actual aerosol from precipitated or deposited dust. Dusts of mineral origin are of particular interest since they have given rise to an industrial problem of some considerable importance. Certain dusts containing silica, either free or combined or in both these states, when inhaled, cause silicosis and allied pulmonary diseases. Such dusts may be produced by the disintegration of rocks or minerals during processes involving crushing, grinding, drilling, blasting, or, in fact, during any process in which disruptive forces are applied to the material. One of the most important physical factors in the causation of pulmonary disease is the size of particles in the dusts, since only those particles below a certain size can reach the finer passages and air sacs of the lungs and start those changes leading to disease. A fraction of the particles which eventually reach the ultimate pulmonary tissue is deposited. It is probable that this deposition within the lungs is selective and particles of certain sizes are more readily retained than others. Furthermore, the harmful action of the particles after they have been deposited is probably dependent upon particle size. For the successful application of measures for the elimination of dust from air likely to be inhaled by workers, account must be taken of the sizes of particles. The design of exhaust ventilation must be such that the drag on the particles is sufficient to carry them out of the general atmosphere. In filtration of dust from the air, selectivity with regard to particle size plays a part, beside which, such factors as the rate of clogging of the filtering medium by particles of different degrees of fineness have to be considered.

The present investigation was undertaken primarily with the view to determining the sizes of particles likely to cause pulmonary disease, and is concerned with mineral dusts which form moderately stable aerosols mostly containing particles of mean diameter extending from about twenty microns downwards. Particles larger than this size have a high rate of sedimentation and are not considered to be of importance. Determinations have been essentially of an industrial character, but, as the results have thrown some light on the intrinsic nature of dusts, they are worth consideration purely from the standpoint of their bearing on general problems of the formation and behaviour of disintegration aerosols.

Method of Determining Size-Frequency.

Of the numerous methods available for the determination of particle size in aerosols, few are suitable for estimations under industrial conditions. Such methods as the direct estimation of size by measurement of the rate

of fall of particles, either visually or photographically, can only be readily applied in the laboratory. Reliance has, therefore, been placed on the microscopic measurement of the particles after they have been deposited from the dusts. This method is dependent upon the efficiency of the method for precipitating the particles and is limited by the resolving power of the microscope. For deposition, the thermal precipitator, modified from the original design of Whytlaw-Gray and Lomax, has been used.[1] In this instrument the particles are deposited on microscope cover-glasses on either side of an electrically heated wire. Dust-laden air is drawn into the instrument and the particles are deposited in linear streaks above the wire. Provided the rate of aspiration does not exceed 7 c.c. per minute and the wire is heated to a temperature such that the dust-free space surrounding the wire extends across the space between the cover-glasses, precipitation of all particles in the dust is complete between the limits of mean diameter of at least 20μ and about $0\cdot2\mu$ or smaller. In using the thermal precipitator samples may be taken over a period of time varying from a few minutes to several hours. Long period sampling is advantageous under industrial conditions since casual fluctuations in concentration and sizes of particles render samples, taken over a short duration of time, of doubtful statistical value.

The method of determining the size-frequency of particles has already been described in a previous publication [1] and need only be mentioned briefly here. After a sample of the dust has been taken with the thermal precipitator, the cover-glasses are ignited at 500° C. for about ten minutes in order to remove combustible or volatile particles of extraneous atmospheric pollution which are almost invariably present under industrial conditions. When cool, the cover-glasses are mounted dry on a microscope slide. Mounting in a liquid medium would tend to disturb the deposit and break up aggregates of particles which were present as such in the air. Although mounting in air enables the particles to be seen in maximum contrast to their surroundings, it has the disadvantage that it does not permit the fullest use to be made of the resolving power of the microscope.

Examination of particles is done under a magnification of 1500 diameters with a microscope fitted with a 2-mm. oil immersion apochromatic microscope objective and a × 17 eyepiece. For rapidity of working, measurement of particles is made by means of a Patterson comparator graticule [2] set in the eyepiece, the sizes of particles being compared with the known apparent sizes of the discs of the calibrated graticule. It may be noted that a procedure, slightly different from that previously described, has been adopted for the present series of determinations. Instead of stating the diameter of each particle as being equivalent to that of the disc which it most nearly matches, particles have been grouped in small size ranges. According to this method all the particles above a certain size and up to and including another greater size are placed in one group. This enables the limits of size within various ranges to be defined more precisely than by the original method.

It should be emphasised that, owing to diffraction effects, exact measurement of particles below $0\cdot4\mu$ diameter is not possible with the microscope system employed, although the presence of particles $0\cdot2\mu$ diameter or smaller is readily detectable. It should also be noted that the particles, often irregular in shape, are treated as equivalent spheres and, in effect, it is the cross-sectional area of the two-dimensional image which is compared with the disc in the comparator graticule. If the particles are plate-like in form, the method may give rise to an over-estimation of sizes of particles, considered as spheres, since such particles tend to be deposited with their larger surfaces parallel to the cover-glasses. When particles, such as those

[1] Green, H. L., and Watson, H. H., *Medical Research Council, Special Report*, No. 199 (H.M.S.O., 1935); Green, H. L., *Bull. Inst. Min. Met.*, No. 362, 1934.
[2] Green, H. L., *J. Industr. Hyg.*, 1934, **16**, 29; Patterson, H. S., and Cawood, W., *this discussion* p. 1084.

of asbestos, have a pronounced fibrous form, it is better to make two distribution counts, one of the length and the other of the diameter of the particles.

Results.

Samples were taken in various industries which provided examples of sandstone, flint, hæmatite, shale, and asbestos dusts. The nature of the dusts will be described *seriatim* below, together with typical results for the size-frequency of particles. The size-frequency depends not only upon the nature of the dust, but on the precise conditions under which the dust is being formed, on the age of the cloud and on the distance from the source of production that the sample is taken. Owing to the existence of particles in dust clouds which have a relatively high rate of sedimentation, the size-distribution of particles is altering continuously with time. Thus size-frequency is very susceptible to changes in local conditions. It is not intended to describe in detail how size-frequency varies with different processes, but rather to give a general idea of size in relation to the nature of the dust producing material and the disruptive forces coming into play.

(a) **Flint dust**, produced in milling calcined flint (chalcedonic silica) containing about 96 per cent. silica.

Median diameter of particles: 0.8μ to 1.3μ; 20 to 30 per cent. less than 0.5μ; 70 to 80 per cent. less than 2μ; 1 to 6 per cent. above 5μ.
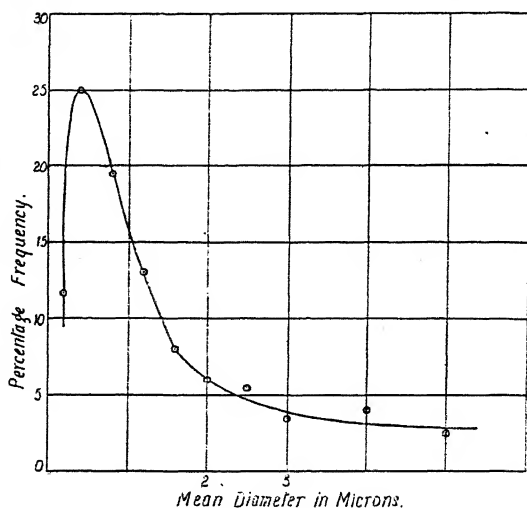
FIG. 1.—Size-frequency curve for particles in a sandstone dust.

(b) **Sandstone dust**, produced in shaping blocks of white sandstone by blows of a mallet on a cold chisel. This was a moderately fine-grained, highly felspathic sandstone containing subangular grains of quartz.

Median diameter of particles: 0.6μ to 1.1μ; 25 to 45 per cent. less than 0.5μ; 70 to 90 per cent. less than 2μ; 1 to 8 per cent. above 5μ.

(c) **Hæmatite dust**, produced in blasting operations in a hæmatite mine; the hæmatite contained 80 per cent. of ferric oxide, 11.7 per cent. of silica, and 0.5 per cent. of alumina. Samples taken from one cloud only.

Median diameter of particles: 0.9μ; 30 per cent. less than 0.5μ; 82 per cent. less than 2μ; 1 per cent. above 5μ.

(d) **Shale dust**, produced in drilling and blasting operations in a hard heading in a coal mine; a hard, close-grained shale containing 29 per cent. of free silica.

Median diameter of particles: 0.4μ to 1.2μ; 25 to 55 per cent. less than 0.5μ; 65 to 92 per cent. less than 2μ; 1 to 10 per cent. above 5μ.

(e) **Asbestos dust**, produced in handling, disintegrating, carding and weaving asbestos. Samples derived from amosite, chrysotile and crocidolite varieties of asbestos have been examined.

Median length of fibres : 2·5μ to 3·5μ ; 8 to 15 per cent. less than 1μ ; 65 to 75 per cent. less than 5μ ; 87 to 90 per cent. less than 10μ.

Median diameter (thickness) of fibres : about 0·55μ ; 43 per cent. less than 0·5μ ; 82 per cent. less than 1μ ; 98 per cent. less than 2μ.

In addition to asbestos fibres in the samples, there was present about an equal number of ordinary dust particles derived from impurities in the asbestos. Various impurities are known to exist in asbestos, as mined, and may consist of talc, serpentine, magnetite and carbonates of calcium and magnesium.[3] The size-distribution of these other mineral particles was as follows : Median diameter : 0·45μ to 0·8μ ; 30 to 55 per cent. less than 0·5μ ; 87 to 98 per cent. less than 2μ ; 1 to 4 per cent. above 5μ.

Detailed figures for certain specific samples are given in Table I. Fig. 1 shows a typical size-frequency curve for a sandstone dust, the sizes being determined in this case by the matching method and not by the grouping method.

TABLE I.—SIZE-FREQUENCY OF PARTICLES IN VARIOUS MINERAL DUSTS.

Size Group. (Microns).	Percentage Frequency for Various Dusts.				
	Sandstone.	Flint.	Shale (during Drilling).	Shale (after Blasting).	Hæmatite (after Blasting).
Up to 0·2	13·6	9·3	7·6	10·0	9·9
0·2- 0·4	14·3	15·7	13·6	10·5	14·7
0·4- 0·8	14·0	14·2	15·6	17·0	19·8
0·8- 1·2	11·3	13·6	10·6	12·5	17·6
1·2- 1·6	10·0	11·3	9·3	9·5	10·8
1·6- 2·0	8·0	9·6	8·0	6·5	8·6
2·0- 2·5	6·6	9·8	7·6	4·0	6·8
2·5- 3·0	6·6	8·2	7·0	10·0	4·8
3·0- 4·0	5·0	4·3	6·6	6·4	4·4
4·0- 5·0	3·3	2·5	3·6	4·6	1·8
5·0-10·0	3·6	0·9	3·0	4·0	0·8
Above 10	3·7	0·6	7·5	5·0	< 0·1

Discussion of Results.

The Sizes of the Particles.

Although the size-frequency of particles may show variations of a fairly large order between one kind of dust and another, the results have features which appear to be common to all kinds of mineral dusts.   One particular feature is the high proportion of particles which are below 2μ diameter, and, in some cases, below 0·5μ.   It is commonly believed that dusts contain a large proportion of relatively coarse particles. Gibbs[4] distinguished between the various kinds of industrial aerosols according to the size of particles, and classified dusts as containing particles larger than 10⁻³ cm. (10μ) diameter, but later,[5] in a modified classification, considered dusts to be disintegration aerosols containing particles greater in size than 10⁻⁵ cm. (0·1μ).   The present results are in conformity with the latter classification and indicate that dusts possess a high degree of dispersion.

[3] Hurlbut, C. S., and Williams, C. R., *J. Industr. Hyg.*, 1935, **17**, 289.
[4] Gibbs, W. E., *Clouds and Smokes*, London (J. & A. Churchill), 1924, p. 130.
[5] Gibbs, W. E., *J. Soc. Chem. Ind.*, 1932, **51**, 1042.

A comparable series of size-frequency determinations was made by Bloomfield [6] in the United States by means of the Owens jet dust counter. Although his results show the same high proportion of particles less than $2 \cdot 0\mu$ diameter as in the present determinations, they show a very much lower proportion less than $0 \cdot 5\mu$. In one case 10 per cent. less $0 \cdot 5\mu$ is recorded and in the remaining twelve cases the highest proportion is $3 \cdot 0$ per cent. These results are somewhat surprising, as it has been shown that the Owens jet dust counter is more efficient in precipitating particles of the order $0 \cdot 5\mu$ than those of 2μ diameter,[7] and the types of dusts were not very different from those recorded in the present series of results. There is a possibility that some of the finest particles were not detected and measured, since the magnification of 1000 diameters used by Bloomfield was somewhat low for this kind of microscopy.

It is of interest to note that the finer particles in dusts cover the same size range as the coarser particles in smokes, which, in general, contain particles of diameter from $0 \cdot 1\mu$ to $1 \cdot 0\mu$. Thus dusts of a high degree of dispersion are comparable with very heterogeneous coarse smokes. It may be noted, however, that fine dusts in an enclosed space have an apparently higher coagulation constant than heterogeneous smokes. The rate of diminution of particles with time follows approximately the law, $dn/dt = - Kn^2$, where n is the number of particles per unit volume at time t and K is a constant. Whytlaw-Gray [8] gives values for the coagulation constant for heterogeneous ammonium chloride smokes ranging from $0 \cdot 55$ to $1 \cdot 70 \times 10^{-9}$ cm.^{3}/sec. Whereas for flint dust clouds, containing particles not greater than $5 \cdot 0\mu$ diameter, values of the order of $6 \cdot 0 \times 10^{-9}$ cm.^{3}/sec. were obtained by the author. These values were derived from counts by means of the ultramicroscope on the particles generated in a dust chamber. The high value of K is probably due to the extreme heterogeneity of the dust; furthermore, the process of coagulation is probably different from that in smokes and is due more to larger particles falling past the smaller ones and colliding with them than to collisions by Brownian motion. It may be noted that the samples of dusts in industry were for the most part taken within a short time of the release of particles which were being continuously generated, and, therefore, the samples were of the primary dust particles. In any case, the numbers of particles in dusts are, comparatively speaking, so low that the actual rate of coagulation is very slow. For instance, if the number of particles in the dust were 10,000 per c.c. (a high value) this would only diminish to about 8000 per c.c. after being left in an enclosed space for one hour, assuming that there were no loss of particles by sedimentation. Hence, aggregation by collision in dust clouds is not usually a factor of importance; such losses of particles that occur are due mainly to sedimentation. When aggregates are found in dusts, they are usually present as such in the original material from which the dust is generated. Re-dispersal of a dust that has been precipitated will often give rise to a cloud containing many aggregates.

A question of some importance is whether particles of diameter less than $0 \cdot 2\mu$ exist to any extent in dusts. An answer of this question has been attempted in several ways, although the results so far obtained are not sufficiently accurate to warrant their publication in detail. Particles generated by impact of a chisel on a block of sandstone in a dust chamber

[6] Bloomfield, J. J., *U.S. Pub. Health Rep.*, 1933, 48, 961.
[7] Green, H. L., and Watson, H. H., *loc. cit.*, p. 19.
[8] Whytlaw-Gray, R., *J. Chem. Soc.*, 1935, 268.

were allowed to settle on collector slides,[9] and were counted under a form of dark-ground illumination according to the method described by Whytlaw-Gray. These counts did not differ sensibly from those obtained by counting particles, which had settled on cover-glasses, with the direct vision microscope. The collector-slide method probably enables solid particles as small as $0 \cdot 1\mu$ diameter to be detected and counted.

Another method has been to count the sandstone particles by means of the photographic Aitken apparatus,[10] which is capable of detecting particles well below $0 \cdot 1\mu$ diameter. In this case the difficulty has been to free the air from atmospheric nuclei which are revealed in the condensation process in the Aitken apparatus and which may far outnumber the dust particles in the air. This difficulty mainly arises when an attempt is made to reproduce an industrial process in a dust chamber of large volume. Again, so far, the results have not shown that particles below $0 \cdot 2\mu$ diameter exist to any appreciable extent in these sandstone dusts.

In certain determinations of size-frequency of mineral particles produced by blasting operations in coal mines, it was noted that there were large numbers of very fine particles which were just visible under the microscope and appeared to be rather smaller than the finest dust particles. Subsequent experiments with the explosive, when fired alone, showed that these fine particles were derived from the explosive itself and not from the rock, *i.e.*, they were incombustible smoke particles. Thus, even when rocks are disrupted with explosive violence, there is no indication that there are many particles formed which are less than $0 \cdot 2\mu$ diameter.

A point bearing on this question is that the size-distribution of particles in dusts tends to follow a probability law. It is true that at the top end of the scale there is a tendency to depart from the law owing to falling out of the larger particles before they reach the sampling apparatus, but, when losses due to sedimentation are not appreciable, the size-frequency curves approximate to asymmetric probability curves of the " cocked hat " type. Thus, distribution of sizes appears to be a purely random one; it may be inferred from the curves that the expectation of producing particles less than $0 \cdot 2\mu$ diameter is small.

On the theoretical side, Gibbs [5] considered that there is a natural limit to the extent to which solids or liquids can be reduced in size by disintegration methods. This limit is imposed by the operation of cohesional or surface tension forces upon each separate fragment of material as it is being formed during the process of disintegration, and he considered the lower limit of particle size for such disintegration aerosols to be of the order of $0 \cdot 1\mu$. Researches on the theory of fine grinding have yielded some information as to the limiting size of particle that can be formed by disintegration processes. In some work on this subject, Martin and his associates [11] did not find any end point to the production of fine particles, but as the smallest particles that were measured had a diameter of $0 \cdot 85\mu$, the results of their experiments must be regarded as being inconclusive. On the other hand, Andreasen [12] estimated the sizes of particles by sedimentation in a liquid medium, and deduced that particles as small as $0 \cdot 1\mu$ diameter could be formed by grinding.

[9] Whytlaw-Gray, R., *loc. cit.*, p. 270 ; Whytlaw-Gray, R., Cawood, W., and Patterson, H. S., *this discussion*, p. 1055.
[10] Green, H. L., *Phil. Mag.*, 1927, **4**, 1046.
[11] Martin, G., Blyth, C. E. and Tongue, H., *Trans. Ceram. Soc.*, 1923, **23**, 61.
[12] Andreasen, A. H. M., *Kolloidchem., Beihefte*, 1928, **27**, 349.

Mechanism of Formation of Dusts.

The size-frequency of particles throws some light on the mechanism of the formation of dusts. The process of disintegration of the mineral or rock is accomplished by the application of shearing and tensile stresses, slowly, as in milling processes, or suddenly, as in drilling with pneumatic drills. The effect of the applied forces is to cause disintegration by splitting or cracking along planes of weakness in the material. It is possible to distinguish between two classes of particles, represented respectively by small fragments, and by fine particles released from the freshly formed surfaces by cracking on a micro scale as the material is torn apart. It is likely that the dusts which were estimated in the present series of experiments belong almost wholly to the latter class. On this theory it is possible to account for the observation that the sizes of particles in dusts formed by explosions are comparatively little different from those of particles formed by less violent processes of disintegration. Explosion entails disruption with extremely high velocity, but in essentials the action is the same as in other disintegration processes, that is, fragmentation takes place with release of fine particles from freshly exposed surfaces. It is true that fragmentation is more complete, but the sizes of the finer particles are similar to those of other industrial dusts.

It would be expected that the size and shape of dust particles would depend upon the mineralogical nature and structure of the material from which they are derived. With the exception of the case of asbestos, the present series of results cannot be regarded as being significant in providing information in this respect. There were so many local factors influencing the samples, that it would not be safe to draw more than generalised conclusions from the estimation of size-frequency. Asbestos, however, provides an example of a mineral in which there are definite planes of cleavage, and the splitting process takes place along these planes, yielding fine fibrous particles.

In the case of rocks containing several minerals of different hardness and crystal size, fracture may occur more readily through some of the minerals than through others, and the composition of the dust may be different from that of the original rock. The results so far obtained have not yielded any real information as to the selective fracture of the different mineral constituents. One difficulty in the way of determining the nature of the dust particles in relation to the nature of the parent rock is that such a high proportion of particles are less than 2μ diameter and, at present, there is no physical method available for identifying the exact nature of individual particles of that size range.

Summary.

Samples of industrial mineral dusts have been obtained by means of the thermal precipitator, and the size-frequency of the particles determined under a microscope of high resolving power. Data for the size-frequency of particles derived from flint, sandstone, hæmatite, shale and asbestos are given. It was shown that most of the particles are smaller than 2μ diameter, but there was little evidence that particles of less than $0\cdot2\mu$ diameter occur in mineral dusts. The dusts are considered as disintegration aerosols of a high degree of dispersion, and the significance of the results has been discussed on this basis. A theory of the mechanism of the formation of dusts has been put forward.

The author is indebted to Mr. H. H. Watson for his co-operation in obtaining samples of the dusts. He is also indebted to the Industrial Pulmonary Disease Committee of the Medical Research Council, on whose behalf this work was undertaken, for permission to publish this paper.

GENERAL DISCUSSION.*

Dr. K. Söllner (*London*) said : Can Mr. Green throw some light upon a closely related problem, which may, I believe, be noticed fairly regularly in clean country fogs, and in the presence of fine, clean stone dust, even after blowing it through a hot flame. The presence of a badly stoppered bottle of $Fe(CO)_5$ in a room may also produce a similar sensation. The odour seems to be fairly independent of the nature of the disperse phase, provided that the latter is chemically inert and that no foreign odorous substances are present. The only very tentative explanation I can so far offer assumes that very fine particles reach the olfactory organ high up in the nose (quite analogous to the case mentioned by Green), and adsorb or dissolve some substance naturally present there : this disturbance of the natural stationary state in the olfactory organ possibly causing a sensation of smell.

Dr. C. G. Addingley (*Cleckheaton*) said : I have been using a method somewhat similar to that described by Green, for estimation of asbestos dust in the atmosphere of an asbestos factory ; an Owens' Jet dust-counter was used, and the cover-glass ignited to remove organic matter. In smoky districts a visible ash deposit is left by the soot particles on the cover-glass after ignition ; the number usually varies between about 30 and 150 particles per c.c., but counting is somewhat difficult and uncertain, as the particles are of about the minimum size which the microscope will resolve. The average size of the asbestos particles varies naturally with the process to which the asbestos is being subjected but, in the measurements I have taken, it is much smaller than that given in the paper. I have always found 50 per cent. or more of the particles $0·5\mu$ or less, 5 to 25 per cent. between $0·5$ and 2μ, 2 to 10 per cent. between 2 and 5μ, and up to 5 per cent. over 5μ.

Dr. R. Lessing (*London*) said he could not agree that the size of particles in dusts formed by explosions differed little from that of particles formed by less violent disintegration. In experiments in a Welsh anthracite mine to study the incidence of silicious dust in various mining operations, he found that the dust produced by drilling the hard shale settled relatively quickly, whilst that released by shot-firing in the same rock remained suspended very much longer. He attributed this to differences in particle size. The dust counts in the air were made with a konimeter, and he admitted that in this instrument particles below a certain size, say $0·5\mu$ were not observable.

Professor K. G. Emeleus (*Belfast*) said : It would be interesting to attempt to find some correlation between the size frequency in dust formed by shattering of crystalline material, and the size frequency in the secondary structure of the crystal shattered. Might there not be a tendency for the dust particles to *be* the actual secondary units in the original substance ?

Professor E. N. da C. Andrade (*London*) said : The words " mosaic " and " secondary structure " have been used in many different senses, and made to include, for instance, the slight changes in inclination which occur at small intervals on the surface of rock salt, and certain other, crystals. There seems no reason why these changes of direction should be sources of weakness, for in general, the more perfect a crystal, the weaker it is, and polycrystalline materials, where the changes of direction are large,

* On the three previous papers.

are very strong.   A system of actual minute cracks, such as those found in diamond, has also been called a mosaic structure, and in such cases it seems highly probable that the cracks should be places of weakness, and that the material should tend to fracture along them.   I do not know what evidence there is for this type of structure in crystals which have been studied in the pulverised state, but Professor Emeleus' suggestion might with profit be followed up experimentally.

Mr. F. I. G. Rawlins (*London*) said : The problem of measuring small particles might be facilitated by using a microscope similar to that developed by Barnard.   Ultra-violet light is used, and the optical system is quartz or fluorite.   It is clear from the Abbe-Rayleigh equation that high numerical aperture is essential and objectives having this feature are now available.

Dr. F. T. Peirce (*Manchester*) said : Has any systematic work been done on the efficiency of filtering as a function of pore and particle sizes ?   This might yield a possible, though hardly a precise, method of determining size distribution, and is of direct interest to questions of filtering, including the retention of dust in the nose.

Mr. A. Dooley (*Birmingham*) said : Has the X-ray powder diffraction method been considered as regards its application to the identification of the constituents of dust and smokes ?   In my experience, the method is satisfactory for particles at least as small as $0 \cdot 5 \mu$.

Dr. W. Cawood (*Leeds*), in reply, said : Dr. Dobson has asked a question about the different laws of scattering of light by small particles mentioned briefly in this paper.   The subject is treated in some detail by Whytlaw-Gray and Patterson in *Smoke* (E. Arnold & Co.), chap. xiii.   Briefly, Rayleigh [1] showed that for infinitely small particles the law was $I \propto r^6$, where I is the intensity of the scattered light and r is the radius of the particle.   Mie [2] has shown mathematically that for particles of diameter greater than one-tenth the wavelength of the incident light, the power will decrease with increase of radius to slightly less than two and will then increase to two when the particle is large enough to become a true reflector. Jobst [3] has extended Mie's theories and simplified them.   Patterson and Whytlaw-Gray [4] have obtained confirmatory experimental proof.

Mr. R. S. Bradley (*Leeds*) (*communicated*) : In the grinding of particles mentioned in Green's paper, the work required to overcome the cohesion, and separate a crystallite into two parts, decreases as the size increases, but the work per gm. of material increases rapidly owing to the increasing number of particles.   There is an increase in the work required for the disintegration of particles of diameter less than approximately 10^{-4} cm., owing to the secondary structure of the solid (lineage or mosaic structure), involving the presence of pores and cracks.   The energy of a " crack surface " is roughly half the true surface energy of the solid, on which depends the work required to disintegrate a perfect crystal, so that further decrease in size after the destruction of the secondary structure, requires a marked increase in work.   This may well set a limit to the size of particles obtained by grinding a solid.

Mr. H. L. Green (*Porton*) in reply, said : The phenomenon to which Dr. Söllner has referred, must, I think, be associated with the filtration of fine particles in the passages of the nose, and I imagine that the explanation offered by him affords a tentative solution of his problem.   Possibly the familiar earthy smell after a light shower of rain in summer may be caused by the impact of the raindrops on the dusty ground and the release into the air of fine dust particles which are subsequently trapped in the nose.   It may be that the solubility of these seemingly chemically inert substances in the tissue fluids is sufficient to cause a sensation of smell.

The discrepancy between the general trend of Dr. Addingley's results

[1] *Phil. Mag.*, 1871, **41**, 107, 441.   [2] *Ann. Physik*, 1908, **25**, 377.
[3] *Ibid.*, 1925, **76**, 863.   [4] *Proc. Roy. Soc., A*, 1926, **113**, 312.

for asbestos dusts and that of mine would appear to be due to differences of method. In the report written by Watson and myself for the Medical Research Council,[5] we gave the results of the tests on the efficiency of various dust sampling instruments, and showed that, for flint dust, the Owens jet dust counter only precipitates about 40 per cent. of the particles, and is apparently more efficient for the *smaller* particles than the *larger* ones. I have not checked the efficiency of the Owens counter for asbestos, but the accuracy of the results with the thermal precipitator has been confirmed by parallel determinations by a sedimentation method on asbestos dusts generated in a dust chamber. In the particular works where the asbestos samples were obtained, the smoke particles, after ignition, left no residual ash, but such ash particles were noted in dusts determinations in other places, especially at Sheffield.

The experience of Dr. Lessing also differs from mine, but as his findings are based on visual observations on rates of settling which, in my opinion, may give rise to misleading conclusions and, on counts with the konimeter, which gives results of doubtful absolute or even comparative value, I do not think they can be regarded as disproving the validity of my own conclusions. It would be of interest if thermal precipitator samples could be taken in the mines where Dr. Lessing made his experiments.

Professor Emeleus has raised a most interesting point which I hope will be followed up by further investigation of the secondary structure of crystals. The remarks of both Professor Andrade and Mr. Bradley also lend support to the view that the size-frequency of the particles may be related to the secondary structure of the crystals from which they are derived.

I have at various times considered using the ultra-violet microscope, as suggested by Mr. Rawlins, but I decided that, unless it is shown that there are in dusts numerous particles below $0·2\mu$ diameter, the gain in accuracy by using an ultra-violet microscope would not compensate for the loss of the speed and general utility of the ordinary visual microscope.

Dr. Peirce raises a question which has hitherto received but little attention, although some theoretical work on it has been done by Albrecht,[6] and it was discussed by Gibbs in his book on *Clouds and Smokes*. The subject is of obvious importance, especially in connection with the protection of workers against harmful dusts by means of respirators, and the general problem of the filtration of dusts in industry. I am doubtful whether filters would be sufficiently selective in their action to enable them to be used for the accurate determination of size-distribution of aerial dispersoids.

In reply to Mr. Dooley, the X-ray powder diffraction method has been used for the determination of the percentage of free silica in rock dusts, notably by Clark and Reynolds[7] in Canada, but the method appears to be limited at present to one or two constituents of the dust.

[5] *Medical Research Council, Special Report*, No. 199 (H.M.S.O., 1935).
[6] *Physikal. Z.*, 1931, **32**, 48.
[7] *Univ. Toronto Studies, Geol. Ser.*, 1935, No. 38, 13.

THE AGGREGATION OF SUSPENDED PARTICLES IN GASES BY SONIC AND SUPERSONIC WAVES.

By O. Brandt and E. Hiedemann.

New optical methods for rendering sonic and supersonic waves visible have been systematically studied in the last four years.[1] O. Brandt and H. Freund [2] tried, *inter alia*, the addition of tobacco smoke to indicate the wave-length of sound waves of frequencies between 6 and 50 k.c. in air enclosed in a tube; they observed an almost instantaneous precipitation of the smoke, the rapidity of which was the more astonishing as other observers of the coagulation of smoke by supersonic waves of lower frequency (*e.g.*, H. S. Patterson and W. Cawood [3]) found only very much smaller effects. We thought, therefore, that further studies on the process of rapid precipitation should be of interest.

Photomicrographic and Kinematographic Observations.

The nature of the process was not immediately evident. Microscopic observation showed suspended particles of some size; this proved that aggregation had taken place in the sound field. More information was secured when photomicrograms of the suspended particles were obtained. The use of kinematographic methods yielded especially significant results. In these experiments it was necessary to obtain photomicrographs with very short times of exposure ($1/125$ second) in order to distinguish between that movement of the particles due to the general circulation between node and anti-node and that due to the oscillation. This was accomplished with the optical arrangement shown in Fig. 1. S represents the end of vibrator rod. R is a vertical sounding tube containing air to which tobacco smoke was added. An observation chamber K made from two ordinary cover-glasses sealed to a celluloid frame of 0·7 mm. thickness was fixed on the bottom of R. Light from an electric arc L was concentrated by a condenser K_0, a diaphragm B serving to screen the central rays. The aperture of the objective of the microscope must be the same as that of the rays screened by the diaphragm, so that no direct light, but a maximum of the light diffracted by the suspended particles, can enter the microscope.

[1] E. Hiedemann, *Nature*, 1935, **136**, 337; *Z. Physik*, 1935, **96**, 273; *Ergebn. exakt. Naturwiss.*, 1935, **14**, 201; E. Hiedemann, H. R. Asbach and Ch. Bachem. *Nature*, 1934, **133**, 176; *Z. Physik*, 1934, **87**, 734 and **88**, 395; E. Hiedemann, H. R. Asbach and K. H. Hoesch, *Naturwiss.*, 1934, **22**, 465; *Z. Physik*, 1934, **90**, 322; E. Hiedemann and Ch. Bachem, *Z. Physik*, 1934, **89**, 502 and **91**, 418 and 1935, **94**, 68; E. H. Hiedemann and E. Grossmann, *Z. Physik*, 1935, **95**, 383; E. Hiedemann and K. H. Hoesch, *Naturwiss*, 1935, **23**, 511, 577 and 705, and 1936, **24**, 60; *Z. Physik*, 1935, **96**, 268 and **98**, 141; E. Hiedemann and N. Seifen, *Z. Physik*, 1934, **91**, 413; Ch. Bachem, *Z. Physik*, 1934, **87**, 738; H. Falkenhagen and Ch. Bachem, *Nature*, 1935, **135**, 830, *Z. Elektrochem.*, 1935, **41**, 570.
[2] O. Brandt and H. Freund, *Z. Physik*, 1934, **92**, 385, and 1935, **94**, 348 and **95**, 415; *Z. physik. u. chem. Unterr.*, 1935, **48**, 259; *Blätter Untersuchungs. und Forschungs-Instrumente*, 1935, **9**, 57.
[3] H. S. Patterson and W. Cawood, *Nature*, 1931, **127**, 667.

Fig. 2 represents the circuit of the vibration generator. The vibrator rod (made of Indilatans-steel) was initially magnetised by means of the coil L_2 carrying direct current. Fig. 3a gives a photomicrograph of the particles immediately after the generator begins to work; the particles are oscillating under the influence of the sonic waves and appear therefore as small streaks with more intensive ends. The length of the streaks is determined by the amplitude of oscillation of the particles.[4] The time of exposure was 1/125 sec. Fig. 3b shows the particles half a second later; the particles of the smoke have in the meantime become so much enlarged by aggregation that their inertia inhibits noticeable oscillation. The time of exposure for this photomicrograph was 1/10 sec. so that the tracks of the moving particles are marked. The coalescence of two or more streaks shows the continued coagulation.

Fig. 4 shows a series of photomicrographs selected from kinematographic observations. Fig. 4 (a) shows the suspended particles before the sonic waves are produced; Fig. 4 (b) taken immediately after switching on the generator, the oscillation of the particles is observed. Figs. 4 (c) to (f) show different phases of the process. Figs. 4 (g) and (h) were made after disconnecting the generator. A comparison of these last

FIG. 1.—Photographic arrangement.
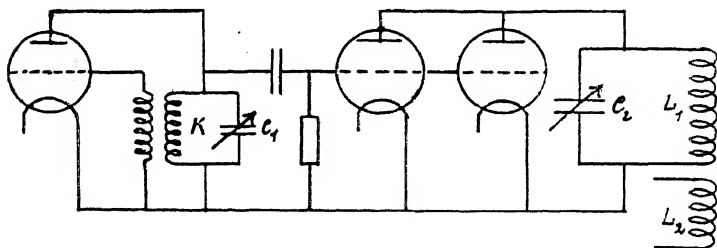
FIG. 2.—Vibration generator circuit.

two pictures with the first indicates the increase in size of the particles. The time of exposure for each picture of the series was 1/25 sec. Whereas the non-coagulated particles practically remain at the same place during that time (they are photographed as points), the coagulated particles cross nearly the whole range of vision.

[4] E. N. da C. Andrade (*Physic. Soc., London, Report of a Discussion on Audition*, 1931) first pointed out the possibility of measuring the intensity of the sound field by the amplitude of the oscillating particles.

These and many other photographs, as well as supplemental subjective microscopic observation, led us to distinguish two principal phases of the process. In the first phase the particles oscillate under the influence of the sound waves and take part in the general circulation between node and antinode, increasing in size by aggregation which takes place in the sound field owing to collisions of the particles. In the second phase the particles are so much enlarged, that they no longer oscillate, but describe very complicated and irregular tracks, similar to those observed by Andrade with particles of cork at lower frequencies.[5] During the second phase the process of coagulation continues by collisions between the enlarged particles and also between enlarged and still oscillating particles.

Measurements of the Rate of Increase in Size of the Particles.

The extent of the increase of the size of the particles under the influence of the sound field was determined by different methods. The measurement of the velocity of the falling particles gives accurate information on the mass of the particle in the case of spherical particles if the Stokes - Cunningham formula is used ; if the particles are not spherical the information so obtained is less reliable, but in most cases gives the order of magnitude. In view of the aniso-dispersity of the aerosols we only measured the velocities of the largest or most rapidly falling particles ; the results of the measurement do not constitute therefore an average of the rate of enlargement, but are none the less significant.
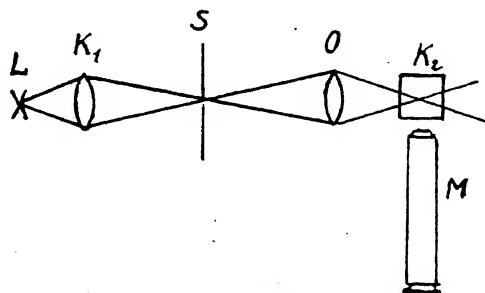
FIG. 5.—Optical arrangement (S. and Z.).

Of course, the range of vision must be sufficiently large for the observation of a considerable number of falling particles, so that the identification of the largest particles does not offer any serious difficulties. For various reasons the observation chamber and illumination applied in the photographic work could not be used. The optical arrangement of H. Siedentopf and R. Zsigmondy (Fig. 5) seemed to be most suited for these measurements. The objective O projects a reduced image of the slit S into the observation cell K_2. The space traversed by the falling particles was well defined by two horizontal threads in the microscope. To avoid disturbances by currents of air in the observation chamber a special double cell K was used (see Fig. 6). The falling particles enter the cell K_1. The illuminating band of light passes first through the window F, which is covered by a glass G_1, into K_1 and then through the glass G_2 into the chamber K_2 where it is absorbed at the opposite blackened wall. In the direction of observation the cell is covered by a cover-glass. All walls which could cause disturbing reflections are suitably blackened. Fig. 7 shows how the observation cell is fixed to the sounding tube.

As it was desirable to measure many particles successively the time of fall was registered by a Morse apparatus. The Morse-key was pressed as long as the particle moved from the upper to the lower thread in the microscope. The time could be determined from the registered lines with great accuracy by a simple arrangement which printed marks on the same

[5] E. N. da C. Andrade, *Phil. Trans.*, 1932, **230A**, 413 ; *Proc. Roy. Soc.*, 1931-32, **134A**, 445.

paper at regular and known time-intervals. The different intensities of the sound field could be compared by measuring the amplitude of oscillation of the end of the vibrator rod. This was done by adjusting a microscope to an illuminated point on the surface of the end of the rod ; when the rod is oscillating the point appears as a line, the length of which can be determined by a micrometer in the eye-piece of the microscope.
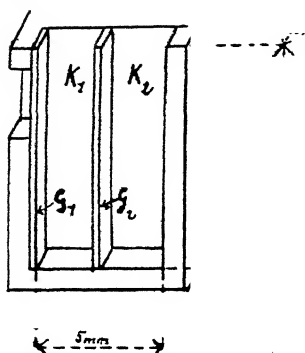
FIG. 6.—Observation chamber.   FIG. 7.—Sounding tube.
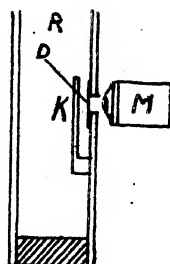
Table I. shows the relationship of the increase in size to the sound intensity ; the first column gives the amplitude of the oscillating rod ; the other column the ratio of the increased mass m to the initial mass m_0 of the particle. In each experiment the aerosol (tobacco smoke) had been under the influence of the sound waves for a time of 5 seconds. Higher intensities of sonic waves were intentionally not used for the measurements. The data of the last column were calculated by the Stokes-Cunningham formula. As to the deviation of the coagulated particles of tobacco smoke from spherical shape see below.

TABLE I.

Amplitude of the Vibrator Rod in mm.	Ratio of the Increased Mass m to the Initial Mass m_0, (m/m_0).
0	1
9×10^{-3}	2·1
18×10^{-3}	8·7
36×10^{-3}	13·6
54×10^{-3}	200

TABLE II.

Time Elapsed after Connecting the Generator in Seconds.	Ratio of Increased Mass m to Initial Mass, $m_0 : m/m_0$.
1	4
2	13
10	110

More reliable results may be obtained by using an aerosol in which liquid (and therefore strictly spherical) particles are suspended. By dispersing paraffin oil a fog was produced, the concentration of which was only 1/7 of that of the tobacco smoke used. Table II. represents some results obtained with this aerosol, and shows how the increase in size depends upon the length of the time during which the sonic waves operated on the system. In all measurements the amplitude of the vibrator rod was 36×10^{-3} mm.

The dependance of the increase in size of the particles upon the intensity (Table I.) proves that with increasing intensity the process may be expected to be highly efficient. Such experiments were successfully made
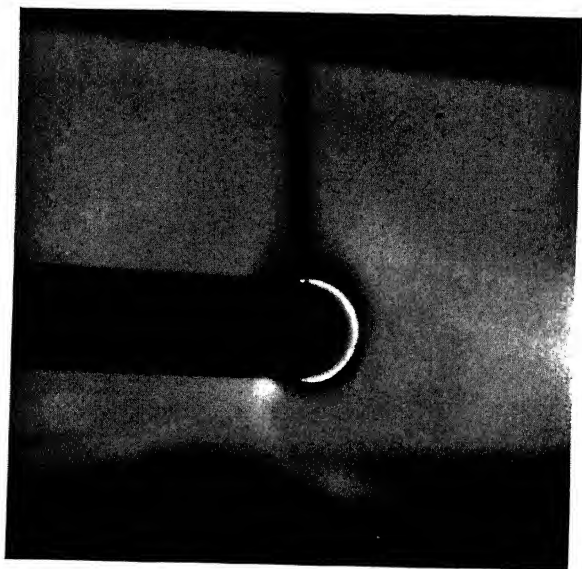
Fig. 2.—Photograph of dust-free space surrounding a hot rod in sulphur smoke. Inner very dark portion is true dust-free space. Secondary semi-dark space is due to evaporation effect referred to on page 1075.
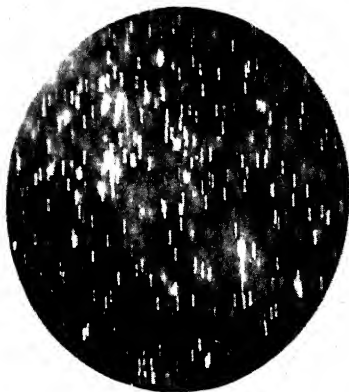
FIG. 3a.

FIG. 3b.

Frequency, 10 k.c.

Size of oscillating particles : Fig. 3a
~0·015 mm. ; Fig. 3b, ~0·045 mm.
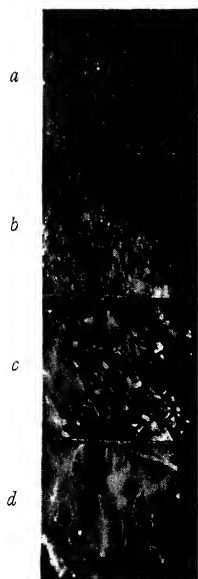
FIG. 4.
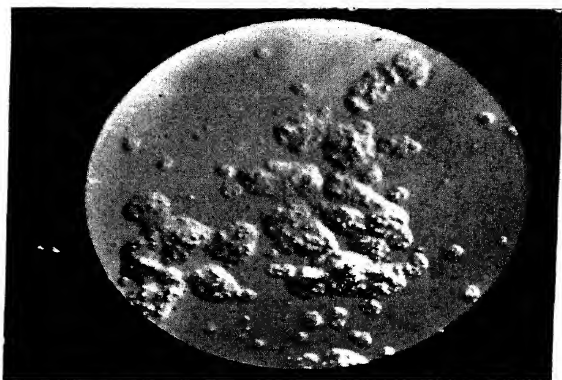
FIG. 11.—Tobacco smoke.

FIG. 12.—NH₄Cl (after).

(× 70)
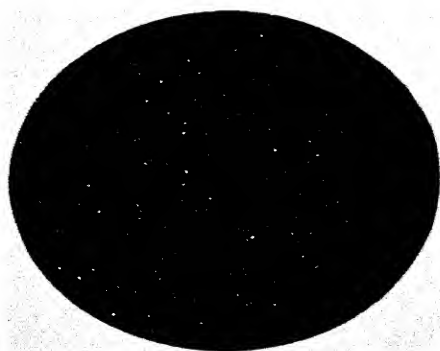
FIG. 13.—NH₄Cl (before).

(× 70)

[*See pages* 1107 *and* 1108.

Fig. 1.—MgO.
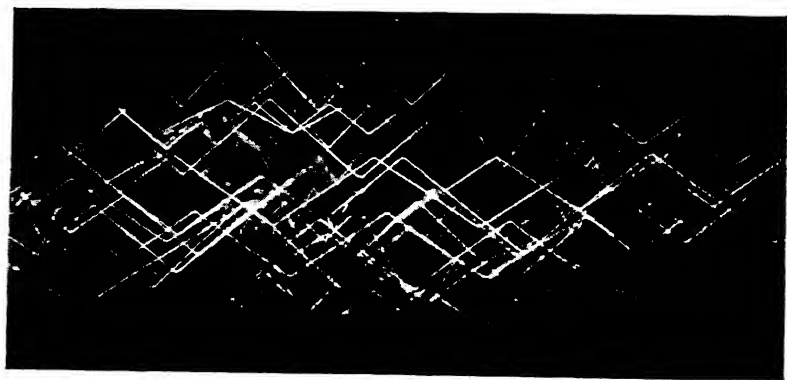
Plate 1.

by means of the air-jet-generator and a powerful magnetostriction-generator and are described below.

Optical Measurements.

Whereas the above measurements give information only as to the increase in size of the largest particles present, one may obtain results as to the average by using nephelometric methods. The high aniso-dispersity which is rapidly brought about under the influence of the sound waves permits only somewhat rough results. Since increase in size under the influence of the sound field is a rapid process, it is necessary to use an arrangement allowing a record of instantaneous changes of the optical properties (the absorption of light) of the aerosol. This condition could be realised by measuring the intensity of light with a photo-electric cell connected to a Galvanometer (Moll) of a very short period of oscillation (1/50 sec.). The deflection of the galvanometer was recorded on a rotating film. The absorption was measured by applying a differential circuit containing two photo-electric cells, represented by Fig. 8. Light from
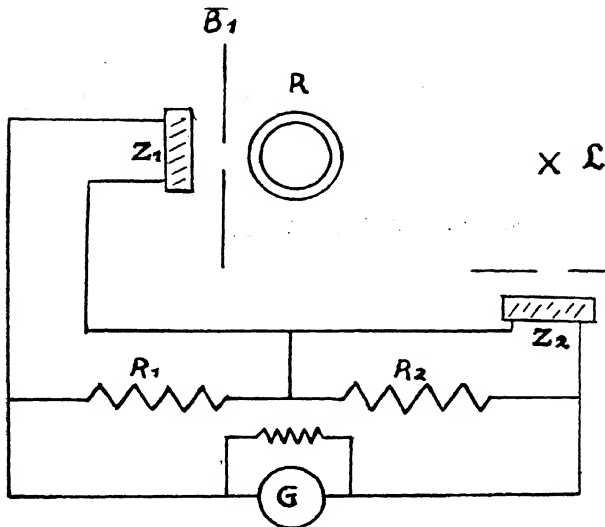
Fig. 8.—Circuit for Nephelometric measurement.

the source L is made parallel by a large (150 mm. diameter) lens (not shown in the Fig.) and then caused to traverse the sounding tube. A similar lens (not shown) forms an image of the source on the diaphragm of the photo-electric cell. A broad beam of light was chosen in order to have several nodes and antinodes in the observed region and to eliminate the influence of local air currents. From the same source, L, light also enters the photo-electric cell Z_2 through the diaphragm B_2, which has a variable aperture. The electric differential circuit is so simple that it needs no explanation. The aperture of the diaphragm B_2 is varied until the galvanometer gives no deflection when there is no aerosol in the tube. When aerosol is brought into the tube the galvanometer deflection increases with increasing absorption of light. By means of neutral tint glasses (the absorption of which was well known) it could be shown that the deflection of the galvanometer was proportional to the absorption of light.

The absorption of light by suspended particles of large size can very approximately be calculated if one considers only the geometrical shape

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of the particles which are supposed to be opaque.[6]   The coefficient of absorption is then given by $n . q$, if n is the particle-concentration and q the cross-section of a particle.   O. Werner [7] has experimentally proved that this theory of G. Mie gives very satisfactory results when applied to evaluate practical measurements.   Using the assumptions of Mie he derives the following formula for the extinction E of light :

$$E = n . r^2 . \pi . s . \log e \qquad . \qquad . \qquad . \qquad (1)$$

where s is the length of the path of the light in the aerosol and r the radius of a suspended particle.   For a constant value of r the extinction E is proportional to the particle-concentration.   To obtain the increase in size of the particles by absorption measurements, we must consider that the radius r changes with n.   If the mass-concentration (g./cm.³) at least remains
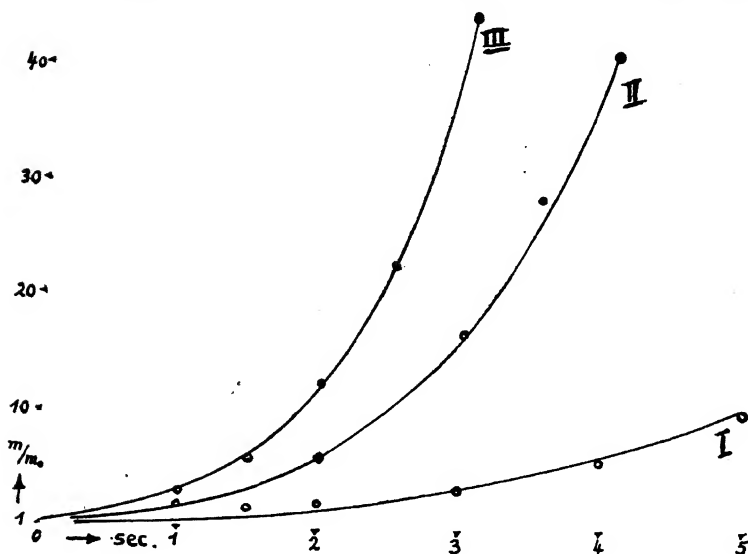
FIG. 9.

constant a simple relation is obtained.   For constant mass-concentration c one gets :

$$c = 4 . \pi r^3 . d . n/3 \qquad\qquad (2)$$

From eq. (1) and (2) one obtains : $E = const./r$ or

$$/E_2 = r_2/r_1 \qquad . \qquad . \qquad . \qquad . \qquad (3)$$

This means that the extinction of light is inversely proportional to the average radius of the particles.   Since this relation is only valid so long as the mass-concentration of the system remains constant, only very low intensities of the sound field could be used.   Fig. 9 shows some results of measurements made with an aerosol consisting of paraffin oil particles suspended in air.   The ordinates give the ratio of the increased to the initial mass and the abscissæ the duration of the influence of the sound field.   The different curves represent different sound intensities.   In curve I. the amplitude of the vibrator rod was 9×10^{-3} mm. and in curve II. 27×10^{-3} mm. and in curve III. 36×10^{-3} mm.

[6] G. Mie, *Ann. Physik*, 1908, **25**, 377.   [7] O. Werner, *ibid.*, 1923, **70**, 487.

The optical method yielded results in good qualitative agreement with the results of measuring the velocity of the falling particles.

Coagulation in Flowing Aerosols.

The rapidity of the acoustical precipitation permitted the study of the process in flowing aerosols. As the rate of coagulation increases with the sound intensity it was necessary to use sonic waves of high intensity. Experiments with powerful magnetostriction-generators using longitudinally divided tubes to which end-pieces of large area were affixed gave very satisfactory results. The extremely simple and efficient source of intense sound waves we have used was the air-jet generator described by Jul. Hartmann,[8] in which a high pressure air-jet is employed which has a velocity greater than that of sound. Along such an air-jet a periodicity of pressure can be observed. If the mouth of a cylindrical pipe is brought to a place where the Pitot-pressure is increasing, very powerful sound waves will be generated in the cylinder, the frequency of which depends, of course, upon the dimensions of the cylindrical resonator. Fig. 10 shows the air-jet generator built into a simple apparatus which has also proved to be convenient for lecture experiments.[9] To two sides of the
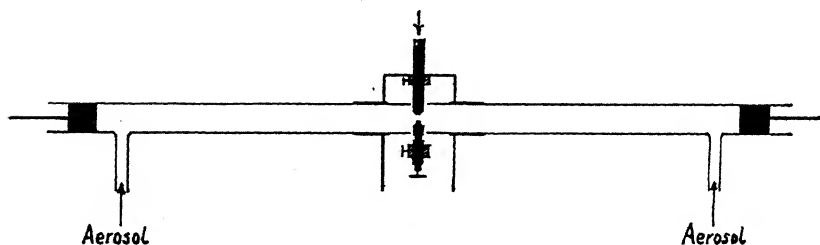
Fig. 10.—Air-jet generator.

generator are affixed tubes (1 metre long and 30 mm. in diameter) which can be tuned by pistons at the opposite ends so that stationary waves will be produced. The aerosol to be studied enters the sounding tubes by means of inlets near the pistons and then flows towards the generator. If the generator is working nearly all the suspended particles will coagulate and be precipitated at the bottom of the tubes. With this simple apparatus somewhat large amounts of aerosols could very efficiently be precipitated : e.g., 200 litres per minute of highly concentrated aerosols such as tobacco smoke or NH_4Cl particles suspended in air. The efficiency of the precipitation was measured by nephelometric methods. Comprehensive studies on the precipitation of many aerosols of a very different nature have been made ; these will shortly be reported elsewhere. Every true aerosol may be coagulated and precipitated in the above manner.

The Shape of the Aggregated Particles.

The above-mentioned evaluation of the velocity of the falling particles and of the extinction of light was based on the assumption that the particles are spherical. For liquid particles this assumption may safely be made. We thought it interesting to study the appearance of acoustically aggregated dry particles such as NH_4Cl and tobacco smoke. Fig. 11 is a photomicrograph of coagulated tobacco smoke. The particles clustered in the gas space have settled down on a cover-glass. The

[8] Jul. Hartmann, *Physic. Rev.*, 1922, **20**, 719 ; *Phil. Mag.*, 1931, **11**, 926. Jul. Hartmann and B. Trolle, *J. Scient. Instr.*, 1927, **4**, 101.
[9] The apparatus was first used in a lecture experiment by E. Hiedemann in the *Haus der Technik* in Essen on the 13th November, 1935.

precipitated particles resemble a very viscous medium in which granular particles are embedded. The drop-like aspect of the smaller particles suggests that their shape in the gas space does not materially differ from the spherical. As has been shown by earlier investigators (see *e.g.*, Whytlaw-Grey and Patterson) one has to expect in dust a non-spherical structure. The high degree of aggregation produced in the sound field leads to a very flocculent structure of the clusters. Fig. 12 is a photomicrograph of NH_4Cl clusters formed by the sound field. The structure is evidently chain-like. Fig. 13 is a photomicrograph of suspended NH_4Cl particles made before the generator was connected. Figs. 12 and 13 illustrate convincingly the extent of the increase in size produced in the sound field. The production of highly aggregated particles by our acoustical method is very rapidly brought about. The application of this method to a comprehensive study of the structure of aggregated particles might perhaps be convenient.

Theoretical Discussion.

The effect of a sound field on suspended particles was first studied by W. König.[10] The work of König was continued with great success by Andrade.[4] S. W. Gorbatschew and A. B. Severny [11] have recently sought to discuss the forces in a sound field which may produce an aggregation of the suspended particles.

A comprehensive theoretical discussion of the process will be given shortly by the authors in another paper. Their theoretical calculations are partly based on the results of König and Andrade and partly on new considerations.[12] It will only be briefly outlined here.

For particles oscillating in a stationary wave the elongation x_{mom} is given by :

$$x_{mom} = A \sin \frac{2\pi a}{\lambda} . \sin \omega t \qquad . \qquad . \qquad . \quad (4)$$

where a represents the distance of the particle from the node, λ the wave-length of the sound waves, $\omega/2\pi = n$ the frequency of the oscillations, and A the amplitude of the particles at the antinode.

The difference between the velocity of the gas particles and the suspended particles, is not great so long as the particles take part in the oscillation. The Stokes' formula may therefore be used to calculate the force operating at any moment on a particle :

$$K = 6\pi r . \eta . \Delta v \qquad . \qquad . \qquad . \quad (5)$$

where η represents the coefficient of viscosity of the gas, r the radius of the suspended particle, and Δv the difference between the velocity of a suspended particle and that of a particle of the gas. From equations (4) and (5) one gets the differential equation :

$$m . \ddot{x} = 6\pi r \eta \left(A . \omega \sin \frac{2\pi . a}{\lambda} . \cos \omega t - \dot{x} \right) \qquad . \qquad . \quad (6)$$

The solution of this equation for the stationary case is given by

$$x = \frac{A . \sin \frac{2\pi a}{\lambda} . \sin (\omega t - \phi)}{\qquad\qquad\qquad} \qquad . \qquad . \quad (7)$$

[10] W. König, *Ann. Physik*, 1891, **42**, 353 and 549 ; **43**, 43 ; *Z. physik. chem. Unterr.*, 1895, **8**, 193.
[11] S. W. Gorbatschew and A. B. Severny, *Kolloid. Z.*, 1935, **73**, 146.
[12] O. Brandt and H. Freund, *Z. Physik*, 1935, **94**, 352, see footnote.

in which d is the density of the particles. The ratio of the amplitude X of the suspended particle to the amplitude G of a particle of the gas is given by :

$$\frac{X}{G}$$

Equation (8) may also be easily derived from the well-known formula given by König [10] by simplifying some expressions in that formula. The simple equation (8) is no less valid than the formula of König but it is much more convenient to handle. It is at once seen from equation (8) that for constant values of d and η the ratio X/G of the amplitudes is determined by the value of $r^2 \cdot n$. If the ratio X/G has a definite value the product $r^2 \cdot n$ has also a definite value which may be calculated by equation (8). In other words a given ratio X/G and a given radius of the particles always correspond with a definite frequency n. The product $r^2 \cdot n$ is therefore a critical relation with regard to the behaviour of the particle in the sound field.

In view of the aniso-dispersity of the aerosol it follows from this critical relation that (for the various suspended particles of the size usually present in aerosols) there always will be found a frequency between 5 and 50 k.c., where suspended particles of different sizes will also have different amplitudes. The difference will become greatest if part of the particles has already been increased by aggregation.

The differences in the amplitudes of the oscillating suspended particles occurring at these frequencies due to the aniso-dispersity of the system may cause the oscillating particles to collide in another and far more efficient way than that considered by Gorbatschew and Severny, who did not take into account the importance of the aniso-dispersity. Calculation of the efficiency of this effect shows that an appreciable amount of aggregation, due solely to these collisions, will occur only at high stages of concentration. Not only are the direct collisions of the particles efficient, however, but even the approach of the particles to one another is of importance, since it increases the probability of aggregation due to other effects. Quantitative calculations of the effect due to this approach of the particles are not yet possible.

The hydrodynamical forces of attraction as considered already by König must also be taken into account. It appears that importance must be attached to the observations of Andrade on vortex formation among particles which do not or only partially take part in the oscillation. Quantitative calculations as to the efficiency of vortex formation have also not yet been made.

The effect of the forces of attraction connected with the pulsation of spheres (studied by Bjerkness) has been considered in the paper of Gorbatschew and Severny. This effect is evidently of less importance with regard to the process of rapid coagulation since dry aerosols, in which no pulsation or a virtual pulsation will take place, may also be precipitated.

High Frequencies.

The above-mentioned experiments were made with frequencies between 5 and 50 k.c., mainly between 10 and 20 k.c. At frequencies of some hundreds of kiloeycles precipitation of smoke can also be observed

as was first reported by E. B. Pearson.[13] The phenomena occurring at the high ultrasonic frequencies cannot be directly compared with those at the frequencies of rapid coagulation. One essential difference is the fact that at these high frequencies not all the particles oscillate ; under certain conditions no coagulation occurs at all. Several particles rotate around another without colliding. Fig. 14 shows the experimental arrangement. Q is the piezo-electric crystal, R is the horizontal sounding tube, and M the microscope. If the microscope is focussed on a layer just above the bottom of the tube the rotating particles can be readily observed as they do not disappear from the range of vision by sedimentation, but move only in a horizontal direction towards the nodes. They appear to be kept at this distance from the bottom by vortices (they disappear at once on disconnecting the ultrasonic generator). The
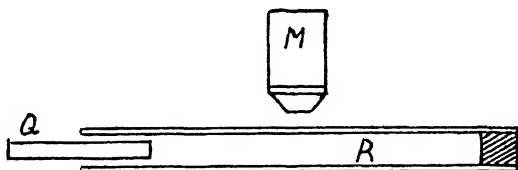
FIG. 14.—Ultrasonic arrangement.

particles moving to the nodes settle down there ; these particles are very small compared with those formed by the process of rapid coagulation. Because of these and other effects the problem of aggregation produced by ultrasonic waves of high frequency needs still further investigation before it seems advisable to communicate any definite results.

Summary.

The process of rapid coagulation by sonic and supersonic waves at frequencies between 5 and 50 k.c. is studied. Photomicrographic and kinematographic observations prove that the process of aggregation takes place in the sound field itself, and give suggestive information about the effect of the sound on the disperse system.

The enlargement of the particles was measured by two different methods. The results show that the particles may easily increase in size more than a hundredfold under the influence of the sound field.

Flowing aerosols may very efficiently be coagulated and precipitated if sufficiently large sound intensities are used.

No complete theory of the process can yet be given, as some of the complex factors cannot yet be calculated quantitatively. It could be deduced that the aniso-dispersity of the system must be taken into account when discussing the process.

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    Universität Köln.*

[13] E. B. Pearson, *Proc. Physic. Soc., London,* 1935, **47,** 136.

THE COAGULATION OF SMOKE BY SUPERSONIC VIBRATIONS.

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In a paper concerning the behaviour of particles in a column of vibrating air [1] I drew attention to the fact that smoke particles in air vibrating at supersonic frequencies would behave much like smoke or other dust particles in air vibrating at sonic frequencies.[2] Later E. B. Pearson, working in my laboratory, carried out some experiments on the subject,[3] and observed a rapid coagulation of tobacco smoke in air subjected to supersonic vibrations ranging from 92 to 801 kc./sec. He found that the coagulated particles formed double lines on the walls of the tube in the neighbourhood of the nodes, reminiscent of the heaps of dust which form to either side of the nodes in the familiar Kundt's tube experiment, and he was able to measure the velocity of sound at supersonic frequencies by means of these nodal figures. Mr. R. C. Parker, who is continuing such experiments, has obtained the phenomenon in a particularly clear manner, as illustrated in Fig. 1, which shows the rings obtained with magnesium oxide smoke at a frequency of 220 kc./sec.

It seems worth while to examine the theoretical aspect of the coagulation. Spheres at rest in a vibrating medium repel one another if their line of centres is parallel to the vibration vector, but attract one another if the line of centres is normal to this direction.[4] The force of attraction or repulsion varies inversely as the fourth power of the distance, and directly as the square of the (maximum) velocity of the vibrating fluid. This attraction of particles suitably placed is sufficient to account in a general way for the coagulation.

The calculations which lead to the results just quoted make many assumptions. In the first place, that the particles are at rest in the fluid, which certainly does not hold with the smallest particles. For instance, at 300,000 $\sim$, for smoke particles, of density $\rho = 1$ and radius $r = 5 \times 10^{-5}$ cm., the ratio w_0/v_0 is 0·182, where w_0 is the velocity amplitude of the sphere and v_0 that of the surrounding air, while for smaller and lighter particles w_0/v_0 will be greater. For the purposes of obtaining an average value of the force for all particles it will, however, suffice to consider the particles as fixed if we take for the maximum velocity of the vibrating air the relative velocity $v_0 - w_0$, in place of v_0. A more serious point is that the calculations assume that the motion of the air surrounding the spheres is vortex-free, whereas under certain conditions, which ordinarily prevail in, for instance, a Kundt's tube, each particle is surrounded by a vortex system which governs the forces between the

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[1] *Proc. Roy. Soc.*, 1931, **131**A, 445, referred to in the present paper as "Circulations."

[2] See in this connection an interesting letter by H. S. Patterson and W. Cawood, *Nature*, 1931, **127**, 667.

[3] *Proc. Physic. Soc.*, 1935, **47**, 136.

[4] Walter Koenig, *Ann. Physik*, 1891, **42**, 353 and 549, and 1891, **43**, 43. Also E. N. da C. Andrade, *Phil. Trans. Roy. Soc.*, 1932, **230**A, 413.

particles.[5] The general explanation of the coagulation is not vitiated even if vortex systems are found, for two particles with transverse lines of centres are still attracted, but the law of force has not been worked out in the case of vortex motion, so that, if it takes place, no attempt at a quantitative theory can be made.

Let us first examine if the assumptions of vortex-free motion can be supported in the case of ordinary smokes. It has been shown [6] that for small spheres the conditions which govern the initiation of vortex motion are expressed by

$$\frac{nad}{\nu} > 4\cdot6$$

where $n = 2\pi f$, f being the frequency of the vibration : d is the diameter of the sphere : a the amplitude of the air vibration : ν the kinematic viscosity of the medium. The smallest spheres for which this law was proved were 0·25 mm. in diameter, and the greatest value of n was 7540, so that in extending it to the supersonic case we are extrapolating beyond our experimental range. There are, however, theoretical reasons for supposing that this extension is justified. The value of $\frac{1}{d}\sqrt{2\nu/n}$, is not very different in the experiments in question and in the supersonic case, and it is apparently only large differences in this quantity, and then in a direction other than that which holds in the present case, that render the extrapolation invalid.[7]

If $f = 100$ kc./sec. and the value of ν be taken as 0·15 (air), then formula (1) gives $ad > 1\cdot1 \times 10^{-6}$: if $f = 800$ kc./sec., $ad > 1\cdot3 \times 10^{-7}$.

If therefore $d < \dfrac{1\cdot3 \times 10^{-7}}{a}$ we need not anticipate vortex motion even at 800 kc./sec., while even for $d < \dfrac{1\cdot1 \times 10^{-}}{a}$ we are safe at 100 kc./sec.

We can make a rough estimate of the greatest value of a from the breaking strength of quartz crystals. Taking this as 9×10^{-10} dyne/cm. (given as maximum value in *International Critical Tables*, **4**, 22) we get for the maximum velocity at the crystal face 700 cm./sec., which at $f = 800$ kc./sec. gives an amplitude of $1\cdot4 \times 10^{-4}$ cm., and at $f = 100$ kc./sec. gives $1\cdot1 \times 10^{-3}$ cm. Owing to resonance these values will be exceeded in the air column, but against this the crystal is never run near amplitudes that lead to fracture normal to the axis. If we take these figures as giving roughly the amplitude of the air vibration, we see that we shall not get vortex motion unless $d > 10^{-3}$ cm. Another factor that will tend to suppress vortex motion with smaller particles is that as the particles get smaller the *relative* velocity of air and particle decreases.

We are justified, then, in assuming vortex-free motion. In this case the force between two spheres each of radius r, at distance d from one another, is given by

$$\left. \begin{aligned} X &= -\frac{3}{2}\,\frac{\pi\rho r^6 w_0{}^2}{d^4}\sin\theta(1 \\ Y &= 0 \\ Z &= -\frac{3}{2}\,\frac{\pi\rho r^6 w_0{}^2}{d^4}\cos\theta(3 - 5\cos^2\theta) \end{aligned} \right\} \tag{1}$$

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[5] *Circulations*, p. 454, *et seq.*   [6] *Ibid.*, p. 463 *et seq.*   [7] *Ibid.*, p. 467.

where θ is the angle which the line of centres makes with the direction of the vibration velocity W. The force is thus proportional to $\dfrac{r^6 w_0{}^2}{d^4}$.

The repulsion which takes place when the line of centres of the particles approaches the direction of the vibration vector need not concern us, as the only effect which it can have on coagulation is a secondary one.

Two particles of the size contemplated, moving together under an attractive force of the magnitude in question, can, in a viscous medium such as air, be supposed to move at a speed proportional to the force and inversely as the surface. The assumption that the resistance is proportional to r^2 is, of course, a provisional one, as the problem of a sphere moving through a liquid oscillating at right angles to the motion has not been solved, to my knowledge. For a sphere simply oscillating in a viscous liquid, however, the component of the resistance which assumes importance for our frequencies and linear dimensions ($n = 2 \times 200$ kc. per sec., $a = 10^{-4}$ to 10^{-5} cm.) is proportional to r^2. The oscillations in our case are, of course, transverse to the travel. The consideration of the accelerated motion of a sphere through the liquid is very complicated, involving as it does $\dfrac{dv}{dt}$ and terms in r^3, r^2 and r. The selection here made of r^2 is justified by the fact that measurements by Mr. Parker, carried out after the calculation had been completed on this basis, agree very well with the formula deduced.

On this assumption the time taken for the particles, of fixed radius r, to move from a distance d until they are in contact, at distance $2r$ between centres, is

$$t = K' \int_{2r}^{d} x^4 dr = K(d^5 - 32r^5)$$

K is a constant during the movement of the particles up to the time when they touch and adhere, but is inversely proportional to $r^4 w_0{}^2$. Let $M =$ mass of smoke per c.c., whatever the concentration, so that we are dealing with the coagulation before an appreciable amount of smoke has settled, and N the number of particles at any moment.

Then mass of single particles $= \dfrac{M}{N} = \dfrac{4}{3}\pi r^3 \rho$

$$\therefore r = AN^{-\frac{1}{3}}$$

where $$A = \left(\frac{3M}{4\pi\rho}\right)^{\frac{1}{3}} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (2$$

The average distance between the particles $= d = N^{-\frac{1}{3}}$. The relative velocity of air and particle, in the case where the particles are not so heavy as to remain fixed while the air washes over them, is

where w_0 is the maximum velocity of the particle during vibration, and v_0 that of the air.

Hence $\tau =$ time in which number N of particles is halved,

$$= BN^{\frac{4}{3}}\frac{1}{v_0{}^2}\left(1 - \frac{w_0}{v_0}\right)^{-2}(N^{-\frac{5}{3}} - 32A^5 N^{-\frac{7}{3}})$$

$$= BN^{-\frac{1}{3}}\frac{1}{v_0{}^2}\frac{1}{\left(1 - \dfrac{w_0}{v_0}\right)^2}(1 - 32A^5)$$

$$= PN^{-\frac{1}{3}}\left(1 - \frac{w_0}{v_0}\right)^{-2} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (3)$$

where P is constant for a given mass of smoke and velocity-amplitude of the air.

Let us suppose that, at the frequency concerned, even the smallest particles with which we deal are not appreciably entrained, *i.e.*, w_0/v_0 is negligible. Then, considering the process as a continuous one

$$\overline{}\,N$$

or

$$dt = - C'N^{-\frac{2}{3}}\,dN$$
$$t = C(N_0{}^{\frac{1}{3}} - N^{\frac{1}{3}}) \qquad . \qquad . \qquad . \qquad . \qquad (4)$$

which gives an initially rapid falling off of number of particles with time, becoming slower as time increases. Fig. 1 represents this law.

Formula (4) gives a coagulation rate which is independent of frequency, because w_0/v_0 has been taken as zero (particles at rest in oscillating medium). Actually, however, w_0/v_0 while exceedingly small for very high frequencies, approaches unity as the frequency diminishes, and it is this that makes rate of coagulation increase with frequency. The factor w_0/v_0 is also a function of the particle size, decreasing as the particle size increases, so that for lower frequencies, where w_0/v_0 is initially not negligible, the curve of Fig. 1 gives a rate of coagulation that is too rapid in the initial stages as compared with the later stages. The quantitative relation is given by the somewhat complicated formula [8]

$$v_0 \qquad \left[\frac{+\,3b\,-}{a^2 + 3ab\,-}\right.$$

Here $a = \dfrac{2\sigma + 1}{3}$, where σ is the ratio of the density of the particles to that of the medium, while $b = \dfrac{1}{r}\sqrt{\dfrac{\nu}{\pi n}}$. For instance with particles of magnesium oxide ($\rho \doteq 0\cdot35$) in air, $a = 200$: with tobacco smoke $a = 820$. With air

$$\overline{\tfrac{1}{2}} = \frac{0\cdot087}{A}\frac{N^{\frac{1}{3}}}{f^{\frac{1}{2}}} = B\frac{N^{\frac{1}{3}}}{f^{\frac{1}{2}}} \qquad . \qquad . \qquad . \qquad (6)$$

In any particular case, therefore, we can find the value of B, and, substituting in (5), obtain w_0/v_0 as a determined function of N and f. If we substitute this in (3) we have a relation between τ and N which involves f and known constants only.

Equation (5) can be simplified only in certain cases, which are best considered as they arise, that is, when particular experiments, with known

[8] W. König, *Ann. Physik*, 1891, **42**, 353. See also E. N. da C. Andrade, *Proc. Roy. Soc.*, 1935, **134A**, 445.

values of B, are in question. It may, however, be pointed out that if $M = 3 \times 10^{-7}$ gm./cm.^{3}, which gives, from (2) and (6), $B = 14.8$ with $\rho = 0.35$: $r = 5 \times 10^{-5}$ cm. initially: $f = 300,000$: then, in (6), $b = 3.2$, and we can neglect $9/2\ b^2 + 9/2\ b^3 + 9/4\ b^4$ in comparison with $a^2 + 3ab$, as amounting to about 1 per cent., and decreasing as coagulation takes place. We can then use the simplified expression

$$\left(1 - \frac{w_0}{v_0}\right)^2 = \frac{\{(a^2 + 3ab)^{\frac{1}{2}} - \frac{3}{2}b\,(2b + b^2)^{\frac{1}{2}}\}^2}{a^2 + 3ab}.$$

In general, however, further simplification is not possible, owing to the values of b being neither small nor great compared to 1.

As an example we may take the following figures, where $(w_0/v_0)_0$, $(w_0/v_0)_{.5}$, and $(w_0/v_0)_{.1}$, represent the initial value and the values after the number of particles has been reduced to one-half and one-tenth respectively. The initial radius r is taken as 5×10^{-5} cm.

$f.$	$(w_0/v_0)_0.$	$(w_0/v_0)_{.5}.$	$(w_0/v_0)_{.1}.$
300,000	0.01	negligibly small	
75,000	0.111	0.050	0.008

This shows that at $f = 300,000$, Fig. 1 should represent the state of affairs without correction. At $f = 75,000$ the initial rate is

$$(1 - w_0/v_0)^2 = 0.79 \text{ times,}$$

and the rate after N has been reduced to a half is 0.90 times, the value given by Fig. 1, the rates for values of N less than 0.1 N_0 being appreciably the same.

Since this paper was first communicated to the Society Mr. Parker has carried out experiments which have confirmed formula (4), and so substantiated the general correctness of the theory.

EXPERIMENTS ON COAGULATION BY SUPERSONIC VIBRATIONS.

By R. C. PARKER, B.Sc.

Professor E. N. da C. Andrade suggested to me that I should look into the question of the coagulation of smoke by supersonic vibration experimentally, with the object of seeing how far the formula which he has derived actually represents the variation of the number of particles with time. The experiment has been carried out with magnesium oxide smoke in air, vibrating at a frequency of 220 kc./sec. In the method used the vibration is allowed to continue for a given time, and the concentration is then determined. The natural coagulation during the period of measurement is negligible, and it has been found possible to reproduce a standard initial concentration with great consistency.

The particle concentration was determined in a manner similar to that employed by Perrin for counting particles in a dilute colloidal solution in his experiments on Brownian motion. The freely suspended particles were viewed through an ultramicroscope fitted with a Zeiss 23·5 mm. achromatic objective, the number visible being that contained in a volume equal to the product of a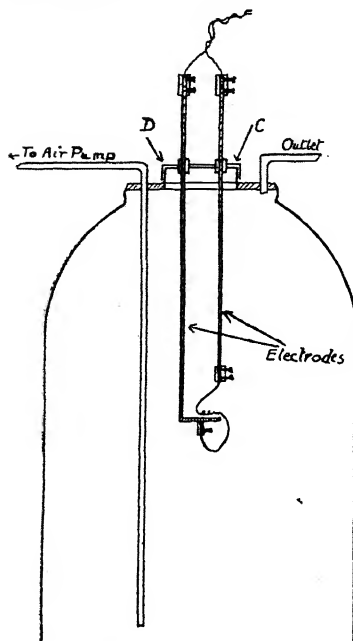 prescribed area of the field of view and the depth of focus of the optical system. In the eyepiece (× 12·5) was inserted a chessboard graticule which enabled the field of view to be restricted within known limits, according to the type of graticule used and the number of squares considered. The concentration was then ascertained by noting the number of particles which could be seen instantaneously in a known volume. A photographic shutter, placed in the path of the illuminating beam, was opened every two seconds for the duration of half a second, and the number of particles noted at each exposure. This number never exceeded 7 or 8. The final values given below (Table II.) represent, for each concentration, the mean of about 720 counts and have a probable error of less than 1 per cent. Only 120 counts were made for any one given filling, after which time the contents of the tube were renewed and the air was set into vibration for the requisite period. Owing to the steady condition of the smoke any local irregularities in its distribution tended to persist over several counts, and hence a more representative value was obtai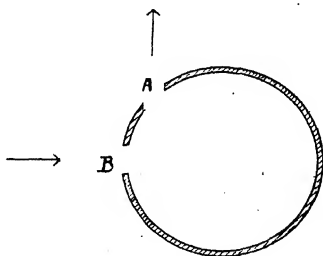ned by selecting for observation each graticule square in rotation. It was found necessary to eliminate any motion of the particles that might arise from convection, otherwise the number of particles seen in the field of view would depend upon their velocity. The several precautions adopted to minimise this source of error are detailed in a forthcoming paper by Andrade and Parker ; they are chiefly concerned with the method of insulating the tube against any local temperature variations, and ensuring that its temperature is that of the entering smoke-laden air.

FIG. 1.

The magnesium oxide smoke was obtained by burning 9·7 mgm. of magnesium ribbon in a stone jar of 12 cubic litres capacity. A diagram of the arrangement used is shown in Fig. 1. A brass cap C, which served to support two long electrodes, fitted closely over an opening in a

FIG. 2.

metallic plate, cemented so as to close the jar. To the lower electrode was fixed an asbestos covered cup on which was placed the requisite amount of magnesium ribbon. Connected across the electrodes, and in close contact with the magnesium ribbon, was a length of resistance wire. The mag-

nesium ribbon was ignited by passing a current through the resistance wire, and filled the jar with smoke.   To determine whether this process gave reproducible results it was repeated six times, the initial smoke con-. centration being each time ascertained by counting.   The values obtained

TABLE I.

Details of count for one determination of the initial concentration.   There were six separate fillings, and three sets of 40 counts were made for each filling.

For fillings 1, 3 and 5 counts were made by observer A.

,,   2, 4 ,,   6   ,,   ,,   ,,   B.

Filling.	1.	2.	3.	4.	5.	6.
Number of particles counted	108	92	109	101	88	101
,, ,, ,,	86	95	102	110	91	82
,, ,, ,,	81	101	107	82	77	94
Total . . .	275	288	318	293	256	277

Total number observed by A   849
,,   ,,   ,,   B   858
Mean number per unit volume   23·7

by two observers, making 360 counts, are detailed in Table I., and, as may be seen, their mean values obtained by the two observers agree to within 1 per cent.   To make certain that, in the absence of a sound field, the normal coagulation and settling under gravity was small, observations were extended over eight minutes, there being exhibited, during this time, no fall in the concentration.

The smoke, on which the above observations were made, was contained in a glass tube of length 16·5 cm. and internal diameter 2 cm.   One end of the tube was closed by a flat glass disc, while the other end was closed by a cylindrical quartz crystal oscillator which fitted with a small clearance all round. Fig. 2 is a cross-section through the tube at the point, 6 cm. from the oscillator, where the observations were made.   The holes A and B were closed by windows of very thin
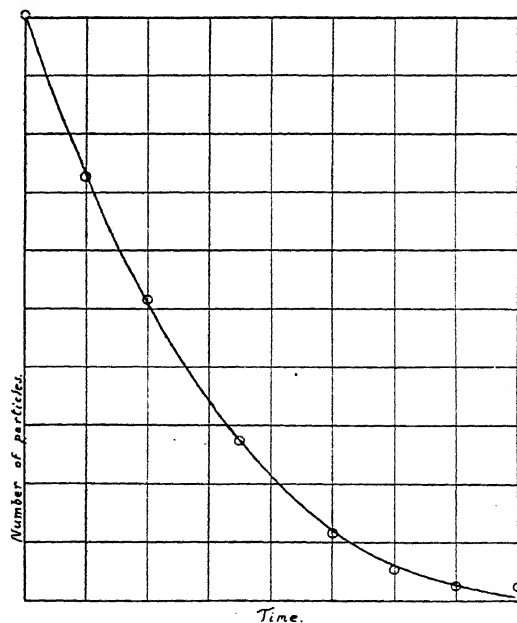
FIG. 3.

glass (the iridescent fragments of a quickly blown bulb) smoothly stuck to the inner surface of the tube, care being taken to avoid any projection which might cause vortex motion.   A pointolite lamp, in conjunction with

a convenient optical system, was employed to illuminate the field of view, and a water cell, 12 inches long, containing a solution of cuprous ammonium sulphate eliminated any heating effect which the beam might have.

The values for the particle concentration were obtained for 8 values of t, the time during which the supersonic vibrations were maintained. The greatest value of t was eight minutes, which caused the number of particles to fall to about 1/40th of the initial value. The eyepiece graticule chosen for the lowest concentration gave an area of observation 16 times

TABLE II.

Time t (Minutes).	No. of Particles per Unit Volume (Each Determination Representing the Mean of 120 Counts).		Mean Value.	Corresponding Values used as Ordinates in Fig. 3.
	Observer A.	Observer B.		
0	22·9 26·5 21·3	24·0 24·4 23·1	23·7	10·0
1	17·1 16·0 14·9 16·2	18·0 15·0 18·9 18·5	16·8	7·28
2	12·6 11·1 12·0	12·5 10·6 14·0	12·1	5·16
3½	6·50 6·64	6·20 6·56	6·47	2·74
5	2·70 2·20	2·90 3·20 2·90	2·78	1·18
6	1·25 1·26	1·45 1·22 1·16 1·50	1·31	0·56
7	0·69 0·62	0·64 0·54 0·63 0·60	0·62	0·26
8	0·60 0·58	0·68 0·57 0·71	0·63	0·27

that used at the highest concentration. Unit volume was taken as that bounded by the graticule square of smallest area, as used in determining the initial concentration. At the very low concentrations, *i.e.*, when the time interval was six to eight minutes, there was a tendency to include certain small non-coagulated particles which were present, and were more obvious when, as occasionally happened, there were no coagulated particles in the field of view. The observations were divided between two observers, whose estimates were in good agreement. As there was usually a number of particles visible, that were not in focus, a certain amount of practice was found necessary : then, ultimately, very satisfactory consistency was obtained.

Table II. gives the values obtained for various times of the coagulating vibration, each value in the fourth column being the mean of about 700 counts. In Fig. 3 is drawn the theoretical relation between the concentration and time, the points plotted being those experimentally determined. The resulting agreement is, as may be seen, extremely close, and there can be little doubt that the mechanism considered in the theoretical treatment, closely corresponds to the existing conditions. Too much reliance must not be placed upon the slight deviation shown at low concentrations, for it is there that the experimental observations become less consistent.

GENERAL DISCUSSION.*

Dr. E. G. Richardson (*Newcastle*) said : The authors have established that there is a range of frequency in the supersonic region most effective for coagulation ; is there not also a most effective amplitude range ? Mr. T. Laidler and I, at Newcastle, measuring the velocity of sound in aerosols, found that coagulation may be to a large extent inhibited, even when using a supersonic source, if the amplitude is kept to a minimum. On the other hand, a large amplitude is known to favour dispersion, as in the production of emulsions by supersonics.

Brandt and Hiedemann have used optical absorption to measure the change of particle size during coagulation, citing the work of Wiener as justification for the assumption that the absorption of light is proportional to the square of the particle diameter. Though this method is very precise, yet I think the results they have obtained from it require correction. Wiener was concerned with transparent particles, *i.e.*, fogs. I have verified the same law for the extinction of light by opaque particles in suspension down to 10μ, yet for diameters between 10μ and 1μ Cheveneau and Audubert [1] have shown that an extinction coefficient proportional to the diameter fits the results better. What was the range of particle size in the present experiments ?

Mr. G. W. Slack (*Leeds*) said : it may be questioned whether any differentiation, in the later stages of coagulation, between coagulated and uncoagulated particles is desirable in what is fundamentally a statistical investigation, since any such distinction must obviously be made on an arbitrary size-basis and since, moreover, it is impossible to say at what time this process should be started. If we count *only coagulated particles* then the number at the start must be taken as zero, whilst on the other hand if we count *all* the particles, then, towards the end, Mr. Parker's counts are admittedly too low and the divergence from the theoretical expression of Professor Andrade will be in the same direction as the results of Brandt and Hiedemann,[2] and also in accordance with the qualitative experiments of Patterson and Cawood [3] who found a distinct tendency for small particles to persist after the major portion had flocculated out.

From the paper it is not clear that the smoke must have been diluted, or otherwise treated in some way, to reduce the number of particles, since on making a cloud of the mass concentration given the numbers fell rapidly from 5×10^7 to 5×10^6 in $6\frac{1}{2}$ mins.

Dr. K. Söllner (*London*) said : Liquid, non-metallic substances are dispersed into gases by the same mechanism as that which causes emulsification in liquid/liquid systems, *i.e.* cavitation, as was shown a short time ago.[4] When the sound travels through the liquid, the latter is stretched locally and disrupts there, forming a cavity. If an external force (*e.g.* gas pressure) acts from outside this cavity collapses vehemently, as was shown by Lord Rayleigh.

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* On the three previous papers.
[1] *Ann. Physique*, 1920, **13**, 134.   [2] *This vol.* (Table II. and Fig. 9).
[3] *Smoke*, Whytlaw-Gray and Patterson, p. 183.
[4] C. Bondy and K. Söllner, *Trans. Faraday Soc.*, 1935, **31**, 835.

Attention should be drawn also to the papers on orthokinetic coagulation by G. Wiegner and co-workers, chiefly Tuorila,[5] who have developed a theory, which takes into account the different velocities of particles of different size, when an external force acts upon the whole system, *e.g.* the different rate of sedimentation in a suspension of particles of different size causes collisions between these particles, thus increasing the rate of coagulation. This orthokinetic coagulation was very helpful in understanding the coagulation of emulsions by ultrasonics,[6] and it may be applied profitably also to gaseous systems.

Mr. A. G. Grant (*Darlington*) said : These very interesting papers on particle coagulation by sonic and supersonic means, open up a wide field of speculation. At the present time there are many simple means of removing coarser particles from gases, and it is the fine particles which introduce complexity and expense. I wonder if sonic coagulation will prove capable of large scale application as a preliminary to electrical precipitation or other known means of particle extraction.

Dr. R. Lessing (*London*) said that Mr. Grant's suggestion that the primary aggregation of particles by supersonic waves might form a first step in the industrial elimination of dispersoids from gases, had an analogue in the addition of flocculating agents to suspensions, which had in recent years been introduced into sedimentation and clarification practice.

Professor R. Whytlaw-Gray (*Leeds*) said : Has Dr. Hiedemann any evidence on the electrical state of the particles during supersonic coagulation ? They may possibly become electrified. Has anything suggesting this been observed ?

The photographs in Dr. Heidemann's paper of the aggregates precipitated by this process exhibit the same structures on a larger scale as those formed in the much slower process of natural coagulation.

Dr. E. Hiedemann (*Köln*) said : We do not agree with Andrade when he attributes the cause of acoustic coagulation only to the forces between spheres in an oscillating medium, as comprehensively studied by Bjerkness.[7] A direct comparison of our results and those obtained by Andrade cannot be made, as the experimental conditions were very different. At the high frequencies he used, the suspended particles do not, in effect, oscillate, whereas at the lower frequencies most of the as yet unaggregated particles oscillate. The conditions at the lower frequencies are much more complicated, as we have seen from our theoretical calculations and our experimental results. The order of magnitude of the effect of the sound field is also quite different. The process of supersonic precipitation studied by Andrade and co-workers takes some minutes to complete, whereas the rapid coagulation by sonic and supersonic waves studied in our experiments needs only a few seconds or less. I will therefore only point out some theoretical points with regard to Andrade's interesting theory. His equation (1) was derived by W. König,[8] who used simplifying assumptions. It is difficult to judge whether these simplifying assumptions are justifiable at the very high frequencies he used, especially where the particle size is so small that molecular discontinuity cannot be neglected for precise quantitative calculations. To approach a solution of the problem it is, of course, justifiable to start with such simplifying assumptions ; for this reason we have also used König's formula in calculating [9] the order of magnitude of the Bjerkness' forces of attraction in the process of coagulation. We preferred to assume the force of the resistance of the medium to the approaching particles to be proportional to r, whereas Andrade has chosen r^2. The law of resistance

[5] Cf., *e.g.*, G. Wiegner, *J. Soc. Chem. Indust.*, 1931, **50**, 55 ; P. Tuorila, *Kolloid-chem. Beihefte*, 1927, **24**, i, 27.

[6] K. Söllner and C. Bondy, *Trans. Faraday Soc.*, 1936, **32**, 616.

[7] V. Bjerkness, *Vorlesungen über hydrodynamische Fernkräfte nach C. A. Bjerkness Theorie*, Bd. 2, 1900-02.

[8] W. König, *Ann. Physik*, 1891, **42**, 353 and 549 ; **43**, 43.

[9] O. Brandt, *Dissert*, Köln., Feb., 1936.

for particles moving at right angles to the oscillation of the medium is as yet unknown, but if one assumes that the motion of particles towards one another is independent of the oscillation of the medium at right angles to that motion, the resistance must be assumed to be proportional to r until somewhat large particle velocities are obtained. If one considers particles of diameter $1\,\mu$, Reynolds' number is smaller than $0\cdot2$, so long as the velocity of the particles is smaller than 600 cm./sec.

The anisodispersity of the system is another serious difficulty, especially as we have seen from our measurements that incipient aggregation has the effect of rendering the system still more anisodisperse. One would also conclude from Andrade's equation (1) that the largest particles coagulate first as the forces of attraction are proportional to r^6, and this would also have the result of making the system more anisodisperse.

In consequence of the large increase in mass of the particles, one would expect an accelerated sedimentation, $e.g.$ similar to that shown in Fig. 1 of the paper. Could the mass-concentration M in equation (2) be made constant ?

Notwithstanding these difficulties, the agreement between Andrade's and Parker's experiments is excellent. But even this cannot suppress another serious doubt. The calculations are made for particles of a strictly spherical shape, but the experiments were made with magnesium oxide smoke. Even if one could assume the primary particles to have an approximately spherical shape, one must consider that after the first aggregation of two particles the enlarged particles are not spherical at all ; for increased coagulation the structure will be very flocculent.

Although one approaches with diffidence the simplifying assumptions of Andrade's theory, the agreement between the theory and the experimental results is so remarkable that one may hope to obtain reliable knowledge of the forces causing aggregation at high supersonic frequencies.

Mr. R. C. Parker (*London*) in reply, said : The distinction made between the coagulated and uncoagulated particles did not play the important part in the observations which Mr. Slack suggests. A few small non-coagulated particles were observed at all stages, and were clearly very different in size, as judged by their brightness, from the main body of particles. After 6 or 8 minutes, when the coagulated particles were very scarce, the smaller particles were comparable in number with the now very much larger particles which were counted. From the point of view of the problem under consideration the uncoagulated particles should clearly not be taken into account. What is in question is not the number of particles, but the number of effective unions, a large number of which go to the making of one larger particle. That the distinction made was not an arbitrary one is clearly shown by the fact that two independent observers, working without any possibility of conscious or unconscious collusion, obtained consistent results.

Mr. Slack has, later, confounded the concentration in the stone jar, in which the smoke was originally produced, with that existing in the observation chamber. The smoke produced in the stone jar was highly concentrated and coagulated rapidly, as would be expected from the work of Whytlaw-Grey and his collaborators. After standing for some minutes, however, the smoke was passed through several pipes and a calcium chloride drying tube, where further coagulation and filtration took place. The result was that the smoke, as initially observed in the observation chamber, had a concentration of 10^5 particles per cm.[3], which did not diminish appreciably in the time concerned. Extremely slow coagulation at this concentration would be anticipated from the work of the Leeds school.

Professor E. N. da C. Andrade (*London*), in reply to Dr. Richardson, said : The variation of coagulation with amplitude is a point of great importance, which has not yet been investigated. According to my ideas the rate of coagulation should vary as the square of the amplitude, and measurements directed to this point would throw valuable light on the

mechanism. No experiments, however, have yet been made in this direction in my laboratory.

As regards the very interesting paper by Brandt and Hiedemann, it is to be regretted that fuller information is not given. We are not told the frequencies which were used, nor, in particular, what precautions were taken against convection, which is generally found troublesome, but which we have eventually succeeded in eliminating. Since, in Fig. 4, the sound was cut off for photographs (g) and (h), and all the streaks are in the same direction, it would appear that convection is largely responsible for the nature of the images. There seems to be no influence that could orient actual long particles all in the same direction. I am also not clear why the exposure was lengthened from 1/125 second for Fig. 3a, to 1/10 second for Fig. 3b. The longer exposure may play some part in the changed appearance. I am a little troubled as to why tobacco smoke particles, which are practically all water, are called dry.

The sketch of the theory is hardly full enough to justify critical consideration. I may say that, for sonic frequencies, I have found, with the assistance of Mr. R. A. Scott, that at 2300 $\sim$, with an amplitude of 0·15 mm., coagulation of tobacco smoke takes place rapidly, (tube practically clear of smoke in 1 minute) whereas at 165 $\sim$, and an amplitude of 1·5 mm., there was no appreciable coagulation due to the sound in half an hour, although the concentration was fairly high. If the forces which I have assumed active in my theory are really responsible for the coagulation this is easily explained, since at 2300 $\sim$ there will be a small relative motion between the air and smoke particles, while at 165 $\sim$ there will be practically none. With the very much greater amplitude which prevails at 2300 $\sim$ than in the supersonic case, a relative motion amounting to only a small fraction of the total amplitude should be sufficient to produce marked coagulation. It is quite possible that these experiments at sonic frequencies are also explicable in general terms on the theory of Brandt and Hiedemann, since at low frequencies all particles, small and great, have about the same amplitude. I am, however, in some doubt as to how their theory can explain the results at high supersonic frequencies, where all particles, small and great, are at rest in the medium. I do not think, therefore, that the aniso-dispersity, which on their theory is responsible for the coagulation, can play any part in the supersonic case, although, of course, both it and the hydrodynamic forces may be active at sonic frequencies. Further experiment is needed on this point.

As regards the criticism of my theory, what is required to test a theory is some kind of quantitative formula which can be experimentally checked, and in the case of a problem as complicated as the present one, some kind of simplifying assumptions are necessary. Those I have made are tentative rather than well established, and I am well aware that subsequent workers may improve upon them. They do, however, furnish some indication of how the problem can be approached. As regards the resistance proportional to r^2, the particle is not moving uniformly but rapidly accelerating, and I have given a rough reason for my adoption of this law. At any rate the application of Stokes' law is clearly not justified. I have actually tried the effect of a resistance proportional to r, and found a formula which disagrees violently with Mr. Parker's observations. This is in itself of some importance, as showing that the experimental results do not agree with practically every likely-looking formula, as might be the case.

I look forward to studying the full theory of Brandt and Hiedemann, especially in its bearing on the variation of rate of coagulation with frequency.

Dr. E. Hiedemann (*Köln*), said: In reply to Dr. Richardson: We have not found a most effective range; we have as yet only observed that the process of rapid coagulation is the more effective the higher the amplitudes. Although large amplitudes of supersonic waves are known to favour dispersion in liquids, such an influence on suspended systems in gases has never been reported.

Our assumption that the absorption of light is proportional to the square of the particle diameter is based upon the work of O. Werner (*loc. cit.*) W. Trabert,[10] G. Mie (*loc. cit.*) and W. Findeisen.[11]

O. Werner has measured the dependence of the absorption of light in fogs upon the particle diameter when the mass-concentration remains constant. The evaluation of his experimental curves in some cases accords with the assumption that under these conditions the extinction of light is proportional to the reciprocal particle diameter, but in other cases the agreement is not good. The different results of Chénevau and Audubert were obtained with suspended particles in liquids and may perhaps not be valid for suspended particles in gases. Most of our particles had diameters from $1 \cdot 6$ to $2 \cdot 0 \mu$. During the coagulation the diameters of the particles increase rapidly to more than 10μ. Even though our assumption should not be quite justified for the smallest particles, only the very first part of the curve would require some correction. The uncertainty of this small and as yet not important part of the curve is unavoidable as different authors cited have got different results. Another and more important uncertainty is due to the aniso-dispersity of the system. But in the evaluation of our measurements both uncertainties may safely be neglected as we only sought information upon the order of magnitude.

In reply to Dr. Söllner : In the short outline of our theory of the process of rapid coagulation we have already mentioned that we have found the anisodispersity of the system to be of importance for the aggregation.[12] The different velocity-amplitudes of the particles of different sizes bring about kinetic impacts leading to coagulation in the frequency range used.

In reply to Mr. Grant : Measurements of the energy required for the process of rapid coagulation by sonic and ultrasonic waves have so far only been made with the usual laboratory apparatus. The efficiency of the apparatus depends of course very much on the sort of acoustic generator used. With a certain generator the efficiency of the sonic aggregation could well be compared with that of electrical precipitation. But the results of experiments on a small scale do not permit definite conclusions regarding large scale application, as one knows many cases in which a chemical process, which is very satisfactory in a test-tube, is quite discouraging when tried on a large scale. It will therefore only be possible to answer this question when comprehensive experimental work has been done on a large scale. We have undertaken such experiments, but some time must elapse before we can give reliable information as to large scale application.

In reply to Professor Whytlaw-Grey : In some cases we have indeed little doubt that the particles precipitated by the process of rapid acoustic coagulation were electrically charged. If, for example, a precipitated aggregate was divided by means of a sharp point, some of the divided aggregate had somewhat strong electric charges. If one moved such charged aggregate through the other aggregates without touching them, forces of attraction and of repulsion could easily be observed. As the experiments on the electric charge of the coagulated, but still suspended, particles are not yet concluded I cannot make any definite statements for this case.

As Professor Whytlaw-Gray points out the aggregates precipitated by the process of rapid acoustic coagulation do exhibit the same structure as those formed in the process of natural coagulation. Since the acoustically produced aggregates are much larger, microscopic study of them may perhaps help to complete the study of the shape of the naturally formed aggregates so successfully made by Professor Whytlaw-Gray and his co-workers.

[10] W. Trabert, *Meteor. Z.*, 1901, 18.

[11] W. Findeisen, *Dissertation*, Hamburg, 1931.

[12] O. Brandt and E. Hiedemann, *Kolloid-Z.*, 1936, 75, 129; O. Brandt, *Dissertation*, Köln, 1936.

Mr. A. G. Grant (*Darlington*) said : From the statements just given by Dr. Hiedemann it looks as if the power for sonic aggregation would be of the same order as that required for precipitation. In this case, as some form of removal plant would still be necessary, the merits of sonic aggregation as an industrial process will be determined entirely by the initial cost of the plant involved.

Dr. E. Hiedemann (*Köln*) said, in reply to Professor Andrade : The measurements and kinematographic observations given in our paper were made at a frequency of 10 k.c., though we have made other observations and measurements over the whole range of frequency of some k.c. to some hundred k.c. As the rapidity of the coagulation at 10 k.c. under our experimental conditions is enormous compared with that studied by Andrade and Parker, convection effects were absolutely negligible, so that we did not need to take any precautions against it. Professor Andrade has misunderstood Fig. 4. What he supposes to be actual long particles oriented all in the same direction are not pictures of particles but of the tracks of the coagulated particles when sedimenting. The tracks of falling particles are of course all in the same direction. From the description of our optical arrangement in Fig. 1 it will be seen that the observation was ultramicroscopic. The reason for choosing different times of exposures in Figs. 3a and 3b is stated in our paper so that this question appears also to be due to the misinterpretation.

In calling NH_4Cl- and tobacco smoke particles " dry " we, of course, only wanted to distinguish between really liquid particles (such as oil drops) and particles consisting of or containing solid or nearly solid matter. The nature of tobacco smoke particles is explained when describing Fig. 11. The opinion of Professor Andrade that tobacco smoke particles " are practically all water " has rather surprised me. Mr. E. B. Pearson working in his laboratory has used cigarette smoke.[13]

On page 139 he states that he has used " smoke, dried by being blown through a long calcium chloride tube." If it were true that smoke particles " are practically all water " I am at a loss to understand what remained in Mr. Pearson's smoke after drying it.

Our theory which is here given only in outline will shortly be published in full elsewhere. We will therefore not deal with the remarks on that outline but will only draw attention to some misunderstandings. We have said that the anisodispersity of the medium is an important factor in the process of coagulation at frequencies between some k.c. and about 50 k.c. (determined by the critical relation $r^2 . n$). But we have not said that this alone is responsible for the coagulation. For the case of higher supersonic frequencies we have given no theory at all, as we want more experimental results before trying to do so. When I pointed out the importance of the anisodispersity of the medium for the case of higher supersonic frequencies I did not of course mean the coagulation effects due to the anisodispersity, which we treat in our theory and which would be called orthokinetic coagulation in the terminology of Wiegner and Tuorila, as Dr. Söllner has remarked. I directed attention to the fact that the forces of attraction in König's equation used by Professor Andrade are proportional to r^6. From this I would conclude that no theory which disregards the anisodispersity of the medium can be expected to give very reliable results. I cannot share the opinion of Professor Andrade as to the law of resistance and I shall treat this question very comprehensively in our forthcoming theory. I regret that Professor Andrade has not indicated how it was ensured that the mass-concentration in Mr. Parker's experiments remained constant.

Professor Andrade's chief objection to my serious doubts as to the reliability of his theory is the agreement between his quantitative formula and the experimental results obtained by Mr. Parker. Mr. Parker's

[13] *Proc. Physic. Soc.*, 1935, **47**, 137.

curve indeed agrees remarkably well with $\dfrac{dN}{dt}$ proportional to $N^{2/3}$ but,

I am troubled by the fact that this formula cannot be derived from Professor Andrade's theory. If one makes the same assumptions as Professor Andrade makes, one really obtains equation (3), but, as a mathematical consequence, one does not get the three next equations given by Professor Andrade. On the contrary mathematical calculations give the following equations :

$$\frac{dN}{N}$$
$$dt = -c'\lambda$$
$$t = e''(N_0^{-1/3} - N^{-1/3})$$

and these equations mean that dN/dt is proportional to $N^{4/3}$. This formula violently disagrees with Mr. Parker's results. That Professor Andrade's quantitative formula is not correct can very easily be seen ; if, for instance, t could be calculated from equation (4), he would get t proportional to $N^{+1/3}$ instead of $N^{-1/3}$. However, I also regard the hydrodynamic forces as important in the case of higher supersonic frequencies.

MEASUREMENT OF THE OPTICAL DENSITIES OF SMOKE STAINS ON FILTER PAPERS.

By A. S. G. Hill.

Estimations of atmospheric pollution are made from stains obtained by drawing known volumes of the polluted air through a restricted area of filter paper. The object of the investigation described in this paper was to determine the suitability of employing a photo-electric density meter to obtain a measure of the optical density of these smoke stains, instead of the more usual visual comparative method involving the use of standard stains. It was desired to relate the stain optical density with the mass of the disperse phase in such stains, and so to estimate the smoke concentration.

Method.

A photo-electric density meter, similar to that designed by F. C. Toy [1] was constructed by modifying the original selenium cell form of the instrument.[2] The selenium cell was replaced by a caesium gas-filled photo-electric cell, with valve amplification. The apparatus is shown diagrammatically in Fig. 1.

Two beams of light from opposite sides of a 6-volt 24-watt electric lamp L were diffused by opal screens, and passed through two optical systems to the photo-electric cell A. A special shutter F enabled the beams (of equal intensity) alternately to illuminate the cell. The photo-electric current produced by the illumination was amplified and balanced as in the usual null method. The stain, the density of which was to be measured, was placed in the path of one beam (at B), and a standard neutral optical wedge W, connected mechanically to a vernier and scale V, graduated in density units, in the path of the other beam of light. The optical wedge was adjusted until the galvanometer G gave a null deflection for either

[1] F. C. Toy, *J. Sci. Inst.*, 1927, 4, 369-75. [2] *Ibid.*, 1924, 1, 362-5.

position of the shutter. The intensities of the two beams alternately incident on the cell were then equal. The reading on the wedge scale was a measure of the optical density of the stain, the units being dependent on the gradation and density characteristics of the optical wedge chosen. The true optical density D (*i.e.* the logarithm of the inverse of the transmission to base 10) for the wedge used in these experiments may be expressed in terms of the scale readings as follows :—

$$D = 0.375 \text{ (Density Reading} - 0.15) + 0.92.$$

The true optical density of a stain (obtained by subtracting the optical density of the filter paper from that of the paper with stain) was 0.375 times the difference between the respective scale readings.

The stains, obtained on a Whatman filter paper (R.F. special), by means of a hand pump (capacity 180 c.c. per stroke), were circular, and approximately 0.60 cm. in diameter. It is essential that the filter paper should be of as uniform density as possible, as variations in the transmission of the paper limit the accuracy of the method.

Samples of the particulate cloud to be estimated were drawn through the filter strips by one or more strokes of the pump until a series of stains of varying densities was obtained for measurement with the density meter. The errors due to paper variations were minimised by examining a series of stains in this manner.

Conditions for the use of the photo-electric density meter should be constant. The lamp current
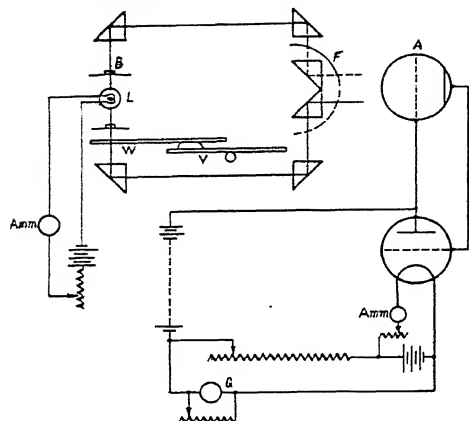
FIG. 1.—Diagrammatic sketch of apparatus.

was maintained at 3.5 amperes, and the valve filament current at 0.25 amperes (Osram D.E. 5B valve, plate voltage 84 volts). After a reasonable time had elapsed for the battery potentials to reach a steady state, the mean optical density of the paper for each strip was measured, and this value used to obtain the optical densities of the respective stains on each filter strip.

A preliminary calibration is necessary for each type of cloud examined. For any given smoke cloud, a series of stains was obtained, and the corresponding concentration of the disperse phase estimated gravimetrically. The concentrations were determined by drawing known volumes of the cloud through small dry asbestos filters, carefully drying the filters, and obtaining the mass increase by means of a balance, sensitive to ± 0.002 mgm. A calibration curve is thus obtained which gives the relationship between the optical density of the stain and the mass of the disperse phase in the stain and hence the cloud concentration.

The concentration of any cloud of the same substance and characteristics may be estimated from this calibration curve by obtaining a series of stains and determining the stain optical densities. Alternatively, if a known concentration C produces a stain density D for n pump strokes, and an unknown concentration produces a stain with the same optical density D for m pump strokes, it follows that the unknown concentration is $\frac{n}{m}C$, since the mass of the disperse phase in the stain must be identical in the two cases.

Results.

1. Coal Fire Smokes.

A small brazier served as the source of the clouds and was introduced into a chamber (approximate volume, 10 cubic metres), for short intervals of time, depending upon the required concentrations of smoke. Fires emitting various amounts of smoke were employed, and dilutions of any cloud were obtained by the admixture of filtered air. The resulting clouds were fanned continuously while mass estimations and stains were obtained simultaneously.

An examination of the particles constituting the cloud obtained from a moderately smoky fire, as used for stain series No. 4 (Table II.), collected by a sedimentation method, afforded the results shown in Table I., for particles visible under the ordinary microscope. Sub-microscopic particles also were possibly present in these clouds. .

Discussion of Results (Coal Fire Smokes).

The relationship between the optical density of stains obtained from coal fire smokes and the mass of the disperse phase in the stains is shown graphically in Fig. 2.

It is somewhat surprising that the clouds from three coal fires burning under different conditions should afford consistent results. Analysis indicated that a very high percentage of carbon was present in these coal fire smokes. Drying the stains had little or no effect on the optical density measurements. The percentage error of the estimation of concentration for individual stains is of the order of $\pm$ 10 per cent. This is mainly due to the variations in the optical transmission of the filter paper. Some difficulty was experienced in obtaining a suitable filter paper of uniform transmission, but the percentage error is reduced to less than $\pm$ 5 per. cent. if a series of stains is obtained and used for the estimation of concentration.

It was found that, with the conditions of these coal fire smoke experiments, the optical transmission of the stain is inversely proportional to the square of the mass of the disperse phase in the stain. It is possible that this relationship exists only for the particular optical arrangement used in the photo-electric density meter. The validity of this method, which is essentially comparative, does not depend upon the accuracy of the optical density measurement.

It is inadvisable to use very dense stains. In practice, it was found necessary to limit the mass of disperse phase in the stain to less than $4 \cdot 0 \times 10^{-5}$ grammes. Inconsistent results have been obtained when this amount has been exceeded. These are probably due to factors governing the transmission of light through such stains. The filter may be affected by strain due to the increased resistance to air flow.

2. Owens' Automatic Recording Air Filter.

This photo-electric method of estimating the density of stains on filter paper was considered of interest in connection with automatic filter records.[3] Dr. J. S. Owens kindly submitted filter discs with various records for examination.

An atmospheric pollution record (Feb. 12/13, 1934) consisted of forty-five stains of various densities, some of which had been assessed shade numbers by Dr. Owens. The maximum variation in the optical density of the filter paper (without stains) was approximately 0·041. These readings were obtained by avoiding watermarks, print and flaws in the paper, the presence of which near or within the stain area would render

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[3] J. S. Owens, *Automatic Recording Air Filter : Technical Methods of Chemical Analysis*, G. Lunge and C. A. Keane, Vol. III., p. 645.

TABLE I.—SIZE OF COAL FIRE SMOKE PARTICLES.

Mean diameter of particles (μ)	0·2	0·4	0·8	1·2	1·6
Percentage of particles	22·7	50·2	20·5	5·7	0·9

TABLE II.—OPTICAL DENSITIES OF STAINS FOR COAL FIRE SMOKES.

Cloud Source.		Smoky Fire.			Moderately Smoky Fire.			Clear Fire (little smoke).	
Stain Series Number.	1.	2.	3.	4.	5.	6.	7.	8.	9.
Concentration mgm./cu. metre.	44·4.	25·8.	10·3.	38·0.	17·6.	6·9.	20·0.	7·6.	3·1.
Number of Pump Strokes — 1	0·30	0·195	0·13	0·29	0·17	0·12	0·19	0·075	0·055
2	0·48	0·30	—	0·46	0·27	—	0·31	—	—
3	0·58	0·39	0·26	0·545	0·35	0·18	0·36	0·18	0·13
4	0·64	—	—	0·64	—	—	0·47	—	—
5	0·75	0·585	0·375	0·675	0·48	0·29	0·52	0·31	0·165
7	—	0·675	0·43	—	0·575	0·35	0·585	0·355	0·205
10	—	—	0·48	—	0·655	0·40	—	0·43	0·24
15	—	—	0·64	—	—	0·53	—	—	0·32
20	—	—	—	—	—	0·59	—	—	0·38
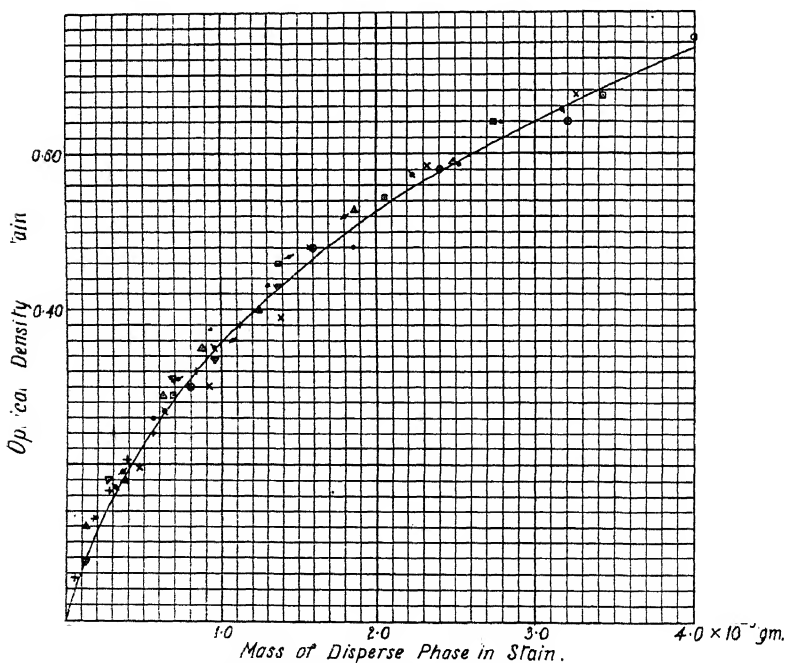
FIG. 2.—Optical density/mass relationship for coal fire smoke stains.

accurate assessment of the optical densities of the stains practically impossible. In the recorder, the filter paper in the region of each stain is subjected to compression. The mean optical density for the compressed areas was 0·026 greater than that for the normal filter paper. This was taken into consideration in estimating the stain densities.

TABLE III.—Owens' Automatic Recording Air Filter Record, DATED 12/2/34.

Stains number 1 to 45 from 00·00 hours.

Stain No. .	1	3	5	7	11	13	15	21	23	25
Optical density .	0·113	0·101	0·064	0·083	0·068	0·071	0·086	0·240	0·248	0·266
Owens' shade number .	4	3	2	2	1·5	1·5	2	10	10	12
Stain No. .	27	29	30	32	33	35	37	40	42	44
Optical density .	0·248	0·266	0·278	0·334	0·413	0·360	0·218	0·135	0·113	0·109
Owens' shade number .	12	13	15	18	20	18	10	5	5	5
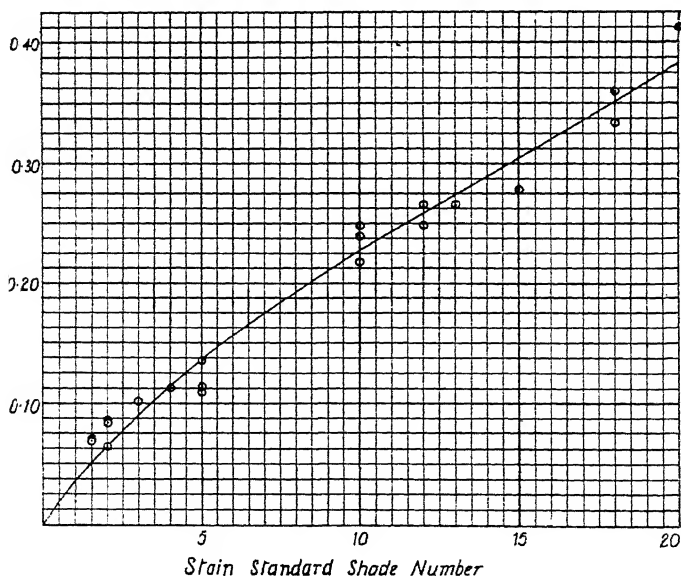
FIG. 3.—Relationship between optical density and shade number for certain atmospheric pollution stains.

The curve showing the relationship between optical density and Owens' shade number, obtained from the results given in Table III., is shown in Fig. 3. It may be observed that the accuracy of the method is of the order of ± 1·5 Owens' shade numbers, the limits of visual assessment presumably being ± 0·5 shade number. The discrepancies shown

in the correlation may be attributed almost wholly to the variation in the optical density of the filter paper used. If a more suitable filter paper were obtainable, having a reasonably constant optical density, a better correlation would result. Alternatively, if it were possible to obtain a larger area of stain, a number of density readings for each stain could be obtained and a mean value would reduce the possible errors of individual readings.

The optical density of the atmospheric pollution stains was more nearly proportional to the mass of the disperse phase in the stain than was the case with coal fire smoke stains. This may be attributed to the different nature of the disperse phase. It is possible that the texture of the filter paper used influences the distribution of the disperse phase in the stain.

The mass of the disperse phase in the Owens' filter stain was compared with that of stains of similar density obtained from coal fire smokes. Owing to the different forms of the two calibration curves, it is not possible to give a constant value for the mass in a stain of unit shade number on the Owens' scale. Thus, a stain of shade number 20 gave an approximate value of 0·29 mgm./cu. metre for unit shade number, while for a stain of shade number 2, a value of 0·26 mgm./cu.m. was obtained for unit shade number. The value given by Dr. Owens for unit shade number is 0·32 mgm./cu. metre.

Although it is not strictly accurate to compare the atmospheric pollution stains with those obtained from coal fire smokes, it may be concluded that the disperse phases in both have much in common, the concentrations required to give a stain of given density being not very different in the two cases.

Application of Calibration Curve to the Estimation of Stain Shade Numbers.

Two filter disc records of atmospheric pollution were supplied by Dr. Owens, the stains of which were not assessed in shade numbers. Density readings were obtained and corresponding shade numbers estimated from the calibration curve. The discs were then returned to Dr. Owens, who kindly assessed his standard shade numbers.

Generally speaking, the results indicated a fair agreement between the visual and photo-electric methods of estimating the stain densities. There appeared to be several anomalous results and, of these, some were definitely attributable to flaws in the paper in or near the stain area. A possible explanation of the remaining cases is that the appearance of the stain by reflected light may not always be a true indication of the mass of the disperse phase in the stain. It is conceivable that an occasional structural variation of the filter may influence the penetration of the disperse phase into the filter. If more of the mass enters the body of the paper, the surface density is decreased and the resulting stain would appear less dense by reflected light than if all the disperse phase remained on or near the filter surface. The photo-electric method, using light transmitted through the stain, would give a measure of the whole mass in the two cases.

Conclusions.

The photo-electric method has proved satisfactory for simple estimations of such coal fire smokes as described. The accuracy of the method is dependent on the uniformity of optical transmission of the filter paper, but with a reasonably good filter paper, and by using a series of stains, the percentage error of estimation of cloud concentration should not exceed ± 5 per cent.

For estimating atmospheric pollution, with the filter discs at present employed, the photo-electric method possesses no advantage over the

visual method. The variations in the texture of the filter papers, and the presence of print, render the photo-electric method liable to error. With a more uniform filter paper, and a larger stain area, the photo-electric method might be used to advantage.

Summary.

A photo-electric density meter has been employed to determine the optical density of stains obtained by drawing known volumes of aerosols through restricted areas of filter paper. The relationship between the optical density of the stains and the mass of disperse phase in them has been determined gravimetrically, and a calibration curve obtained for coal fire smokes. The accuracy of the method is limited by the variations in the optical transmission of the filter paper, but an accuracy of estimation of cloud concentration of $\pm$ 5 per cent. has been obtained by utilising a series of stains for each concentration. The method has been applied to the measurement of the optical density of stains of atmospheric pollution obtained with the Owens' Automatic Recording Air Filter. The Owens' shade numbers and the optical densities of the stains have been correlated and the limits of accuracy of the method have been found to be of the order of $\pm$ 1·5 standard shade numbers. A comparison with stains from coal fire smokes has indicated a similarity in the nature of the stains. Advantages and disadvantages of the two methods have been discussed.

ON THE RATE OF CHARGING OF DROPLETS BY AN IONIC CURRENT.

By N. Fuchs, I. Petrjanoff and B. Rotzeig.

The process of charging floating particles by an ionic current, which plays a very important rôle in the electrical precipitation of smoke and dust, has been the object of a large amount of experimental and theoretical work. This work, however, has been devoted almost exclusively to the study of the final (maximum) charge acquired by the particles in an ionic atmosphere as a function of their size, the applied field-strength, ion concentration, etc. The kinetics of the charging process, on the other hand, have been studied only * by M. Pauthenier [1, 2] and by J. P. Gott.[3]

When the particle is so large that the effects due to diffusion of the ions towards the particle, and to mirror forces, can be neglected, the kinetics of the charging of a spherical dielectric particle can be expressed by the following equation [1] (assuming that each ion striking the surface of the particle gives up its charge) :

$$+ 2^{k} -$$

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* In the work of Arndt and Kallmann [4] we find an investigation of the last stage only of the charging process, when the final charge is practically attained and the rate of charging becomes exceedingly small.

[1] M. M. Pauthenier et M. Moreau-Hanot, *J. de Physique*, 1932, **3**, 590.
[2] Pauthenier et Agostini, *C.R.*, 1934, **199**, 705.
[3] J. P. Gott, *Proc. Roy. Soc.*, 1933, **142A**, 248.

where Q is the charge acquired by the particle in the time t, a the radius, k the dielectric constant of the particle, E the strength of the external electric field, n the number of ions per c.c., u their mobility, and ϵ the electronic charge. For a conducting sphere, the expression $1 + 2\dfrac{k-1}{k+2}$ becomes equal to 3.

Pauthenier and Agostini [2] proved the validity of equation (1) experimentally, using 3 to 4 mm. diameter steel balls, falling freely through a cylindrical electric precipitator, parallel to its axis. The field-strength was measured by these authors by means of an incandescent probe, while n was calculated from the equation

$$n = E/4\pi r\epsilon \qquad . \qquad . \qquad . \qquad . \qquad (2)$$

(r distance from the axis of the cylinder). This equation is well known to be valid for the space where the field-strength is constant. The velocity of fall was determined by photographing the balls under intermittent illumination, and the charge acquired by the balls was measured by means of an electrometer. A very close agreement between the theoretical and experimental values of the charge was found.

In the work of J. P. Gott [3] the ionic atmosphere was produced by means of X-rays, water drops of 4·4 mm. diameter being used, and only the initial rate of charging was determined. The measurements were considerably less exact than in the work of Pauthenier, but nevertheless quite satisfactory results were obtained.

For particles of the order of 1μ radius and smaller (which it is especially difficult to precipitate in practice), the influence of diffusion of the ions and of mirror-forces may, however, be so considerable that equation (1) must be regarded in this case as giving only the lower limit of the rate of charging. The smaller the particles the larger will be the difference between the actual values of the charge and those calculated from (1).

The theoretical calculation of the rate of charging, taking into account the two above-mentioned factors, seems to be exceedingly difficult. The difficulty is especially increased by the fact that the particles under consideration are of the same order of magnitude as the mean free path of the ions. An experimental study of the kinetics of charging in this region of particle size is therefore indispensable.

The ingenious method employed by Arndt and Kallmann [4]—the direct charging of a droplet by ions within a Millikan chamber, periodically interrupting the ionisation in order to measure the charge acquired meanwhile—allows the use of but relatively small field-strengths and current-densities, i.e., of conditions widely differing from those used in industrial electric precipitation. We chose therefore another method, similar to that of Pauthenier. In this method, a narrow air-jet containing floating particles is passed along the axis of a precipitator and thereupon sucked into an ultramicroscopic cell, where the size and charge of the particles are determined. We further used a cloud of uncharged droplets obtained by condensation of oil-vapours, thus avoiding the charges produced on droplets by spraying. It is clear that the rate of charging of a particle in air of the same velocity as itself will be not different from the rate in still air.

[4] Arndt und Kallmann, Z. Physik, 1926, **35**, 423.

Experimental Details.

The general arrangement of the apparatus is shown in Fig. 1. The cylindrical precipitator BCB consists of three sections separated by thin insulating sheets. The outer sections, BB are earthed directly, while the inner section, C made of fine wire-gauze, is earthed through a sensitive galvanometer G. TT are insulating top-plates. The diameter of the precipitator is 31 cm., the total height is 37 cm., and the height of the inner section C is 7·2 cm.

The negative discharging electrode D, made of a silver-wire 0·5 mm. in diameter, is fixed accurately along the axis of the cylinder BCB. The voltage is generated by a transformer connected with a kenotrone and a condenser of 3000 cm. capacity. As we used relatively small currents, of
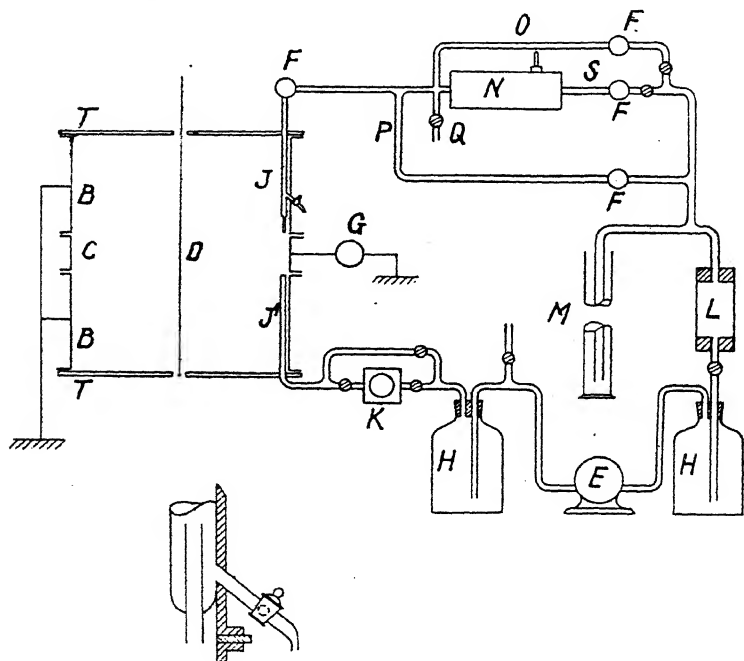
FIG. 1.

about 10^{-5} Å, at voltages of about 30 KV, the smoothing effect of the condenser was very high ; the periodic oscillations of the current, measured by means of an oscillograph, did not exceed 3-5 per cent.

The cloud-jet is let into and out of the precipitator through thin-walled, silver-coated and earthed glass tubes * JJ′, placed strictly along the same axis. The distance from this axis to the inner walls of the precipitator is 0·5 cm. From the tube J′ the charged cloud enters the ultramicroscopic cell K and can be stopped there without interrupting the circulation of the cloud, which is sucked into J′ by means of the pump E. This pump at the same time blows the air through a cotton-wool plug L in the cloud-producer N, which consists of a hollow copper cylinder heated electrically and containing the oil (mineral oil with density 0·91). The hot air-stream

* We could not find sufficiently smooth and thin-walled metallic tubes of the required size.

saturated with oil-vapours mixes with the cold air flowing through the tube O. The cloud produced by condensation is thereupon diluted by the air flowing through P, in order to diminish the concentration of droplets. A large amount of oil condensing on the walls of the tubes is tapped off through Q. This oil was then used for the determination of the dielectric constant * (2·56) and the density (0·895) of the droplets. Varying the rate of flow in the tubes O and S and the temperature of the oil, we could obtain clouds of different particle size, with droplets ranging from 0·5μ to 3μ radius. The droplets settling on the walls of the tube J form an oil layer, which continually flows down and appreciably diminishes the width of the orifice. In order to prevent this, the lower part of the tube was constructed as shown in Fig. 1. The rate of flow in all parts of the apparatus was regulated with stop-cocks and measured by flowmeters FF. HH are air-buffers, and M—pressure regulator.

A number of difficulties had to be contended with, in obtaining a steady narrow cloud jet having practically a constant linear velocity for a length considerably in excess of the diameter of the tubes JJ'. Only in this case could the time of passage of the droplets through the ionic atmosphere be determined with sufficient accuracy whilst, at the same time, the distortion of the electric field caused by the tubes could be neglected.

It was found that, for each width of the jet, there exists a corresponding optimal velocity of flow, at which the jet has the maximum of stability. At velocities considerably differing from the optimal, the jet breaks down at a very short distance from the orifice. We found, further, that very narrow jets widen, i.e., their linear velocity decreases markedly with the distance from the orifice. On the other hand, the scattering of the jet by the ionic current made it impossible to increase appreciably the length of the jet, i.e., the gap between the tubes JJ', and therefore, as already said, to use wider jets.

We finally chose a jet of 3·5 mm. diameter and a mean linear velocity of about 3 metres per second. Under these conditions, the cloud jet, observed in the light of an arc-lamp, has sharp boundaries, and its width measured by means of a horizontal microscope remains constant to within 2 to 3 per cent. throughout its length (5·2 cm.). This shows that the linear velocity remains constant to within 4 to 6 per cent. The whole of the jet is sucked without loss into the tube J' of a larger diameter (8 mm.). To prevent loss, the rate of suction must be appreciably larger than the rate of flow of the cloud in J.

It must be noted that there is a definite distribution of velocities within the jet, apparently similar to that of a Poiseuille's flow, but differing from it by the fact that at the boundary the velocity is not equal to zero. An experimental study of this distribution in such a narrow jet seems to be very difficult, and was not undertaken by us. Its general character can be seen from the scattering of the measured values of charges about the mean values (cf. below). We limited ourselves to the determination of the average velocity from the rate of flow in the tube J and the cross-section of the jet. From this and from the distance between the tubes JJ', we calculated the average time of passage of droplets through the ionic atmosphere with an accuracy of about 5 per cent., the chief error resulting from inaccuracy in measuring the width of the cloud-jet. The error resulting from the fact that a certain number of ions are sucked into the tube J', where they may also be caught by the droplets, must be exceedingly small, as a rough calculation shows.

The jet is naturally made still less steady by the corona discharge, and is deflected from its straight path and dispersed sooner for stronger and stronger current densities. As it was impossible for the aforesaid reasons to shorten the jet appreciably, we were forced to use relatively

* We are much indebted to Mr. V. Vassiljeff who made this determination for us.

small current-densities up to about 10^{-8} Å/sq. cm. The corresponding values of the field-strength and ion-concentration are 1000 V/cm. and $3 \cdot 5 \times 10^{7}$/c.c. The deflection and spreading of the jet, resulting from the charges acquired by the droplets, limits the applicability of the method here described to a study of the initial stage of the charging of droplets in an electric precipitator, namely up to about $\frac{1}{4}$ to $\frac{1}{3}$ of the maximum charge.

The use of small current-densities forced us to employ a precipitator considerably larger than the one used at the first stage of this work (12 cm. diameter). With this we were obliged to have a potential on the discharging electrode differing so little from the starting potential, that the slightest fluctuations in the line voltage caused a marked change of the ionic current. In the 31 cm. precipitator the constancy of the current was quite satisfactory.

The density of the ionic current passing through the cloud jet was calculated from the total current flowing through the inner section of the precipitator. In order to ascertain that the current density was constant throughout the circumference of the section, and not changed appreciably by distortion of the field due to the tubes JJ', a rectangular hole 5·2 cm. high and 1 cm. wide was made in the wall of the section C just opposite the cloud jet. A plate made of fine wire-gauze was inserted in the hole providing narrow air-gaps between the plate and the wall. The plate was connected with the galvanometer G. By measuring successively the current flowing through the whole section and through the plate, we found that the ratio of these currents differed from that of the corresponding areas by not more than 3 to 4 per cent. Thus the reliability of the current density values, calculated as mentioned above, was proved. The accuracy of the current-density measurements can also be considered to have the same value of 3 to 4 per cent.
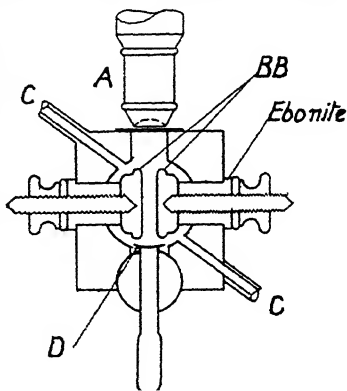
Fig. 2.

Both the size and the charge of droplets were measured in the cell K by the photographic oscillation method worked out in this laboratory [5] as a development of an ingenious idea of Wells and Gerke.[6] The droplets are allowed to fall under the force of gravity and at the same time they are compelled by an alternating electric field to oscillate in a horizontal direction. Photographing the zig-zag paths of the droplets, we can first determine the size of the droplets from their rate of fall, and then their charge from the horizontal velocity * (cf. Plate I., representing one of the photographs made in this work).

The construction of the cell is shown in Fig. 2. It is made from a massive copper block in order to avoid convection currents. A is the illuminating objective, BB the electrodes producing the horizontal field. The cloud is let in and out through the tubes CC. The adjustable spherical mirror D serves to reflect the illuminating beam back in order to avoid the photophoresis of the droplets. The mean error in the determination of charge by this method is about 2 to 3 per cent. for droplets of radius

[5] Fuchs und Petrjanoff, *Kolloid-Z.*, 1933, **65**, 171.

[6] Wells and Gerke, *J. Amer. Chem. Soc.*, 1919, **41**, 312.

* It may be mentioned that in the work of Wells and Gerke one of the motion-components was due not to gravity but to convection or photophoresis. Therefore these authors could determine the charges of droplets only if they knew their size beforehand, or vice versa.
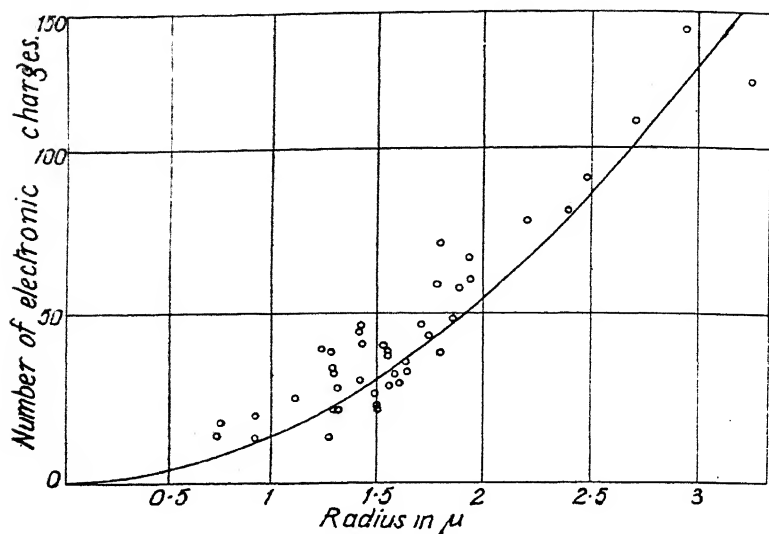
FIG. 3.—$t=$ 0·0165 sec.; $j=$ 3·18 × 10⁻⁹ A/sq. cm.; $E=$ 556 V/cm.; $n=$ 1·98 × 10⁷/c.c.
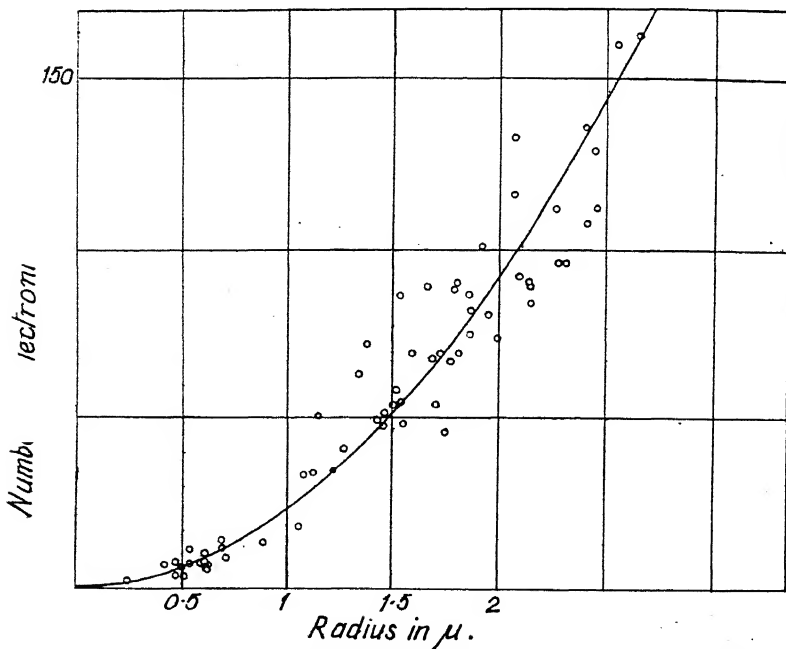
FIG. 4.—$t=$ 0·0172 sec.; $j=$ 5·51 × 10⁻⁹ A/sq. cm.; $E=$ 732 V/cm.; $n=$ 2·70 × 10⁷/c.c.

$> 1\mu$ and about 10 per cent. for droplets of 0.6μ radius (due to the Brownian motion).   The error in determination of the size is about three times less.

A source of error in these ex- periments might be expected in the settling out on the walls of the tube J′ of more highly charged   particles, due to mirror forces and to the mutual electro- static repulsion be- tween   droplets. A rough calcula- tion showed, how- ever, that this cir- cumstance   could not have any prac- tical   significance under the condi- tions of our experi- ments.

The same can be said about the effect due to a screening off of the ionic current by other droplets. As their concentration in the cloud jet was about 10^4 per c.c., the area screened by the droplets of say 2μ radius in

a cloud layer 3·5 mm. thick is only

$$\pi \times (2 \times 10^{-4})^2 \times 10^4 \times 0.35 = 4.8 \times 10^{-4}$$

of the total area.
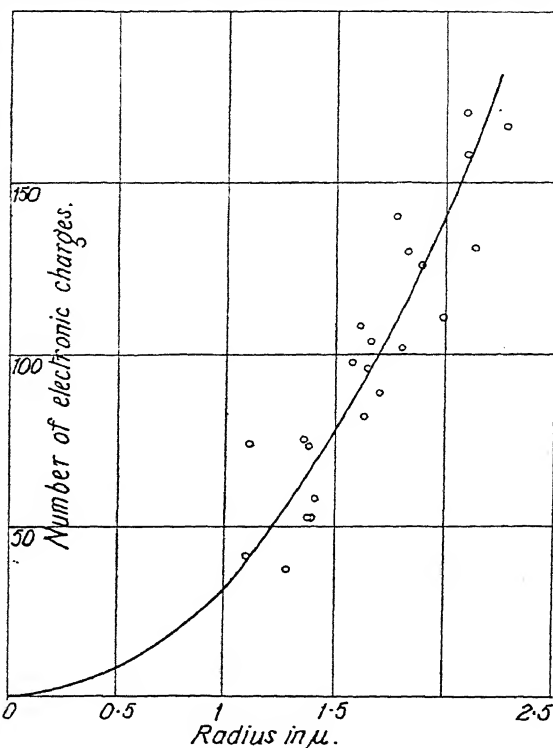
Fig 5.—$t = 0.015$ sec.; $j = 9.1 \times 10^{-9}$ A/sq. cm.; $E = 940$ V/cm.; $n = 3.4 \times 10^7$/c.c.

Experimental Results.

Some of the results obtained in this work are shown in Figs. 3 to 5 The curves are plotted according to the equation

I

derived from (1) by substituting j/E for $un\epsilon$.   ($j =$ current density). The values of t and j are shown below the figures ; k is as large as 2·56. Taking for the mobility of the ions the value 1·75 cm./sec./V/cm. which gave the best agreement between the theoretical and experimental values of the field-strength in the work of Pauthenier and Moreau-Hanot,[1] we obtain from Townsend's equation,

$$E =$$

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corresponding values of field-strength E and ionic concentration n. The error arising from the fact that E was not measured directly, but calculated, could not affect the results appreciably. If, for instance, we take for the mobility the value 1·9 instead of 1·75, the right side of the equation (3) will be reduced only by 1 to 1·5 per cent. The charges acquired by the droplets in these experiments are about 0·2 to 0·3 of the maximum charges.

The experimental points on each curve are taken from several (4-5) photographs. It was very difficult to maintain exactly the same values of ionic current and velocity of the jet in all experiments; they varied as much as about 3 to 4 per cent. In order to be able to put all experimental points on the same diagram, the values of the charges were recalculated according to equation (3).

The scattering of the measured charges about the mean values is due, as already stated to distribution of velocities in the jet, and for smaller particles, besides that to statistical fluctuations.

As can be seen from the diagrams, the mean values of the measured charges lie satisfactorily on theoretical curves. It seems, however, that the data so far obtained are not sufficient to determine definitely how exactly equation (3) holds for the smaller droplets of radius $< 1\mu$. The question will be studied more carefully in this laboratory in the near future.

It must be noted that the method described in this paper is not limited to relatively large particles, whose charge and size can be measured by the " oscillation " or Millikan methods. By measuring the total charge of a cloud by an electrometer and determining the number of particles contained in it, we can measure the charging-rate of particles of any aerosol. This can be accomplished also by measuring the mobility of the charged particles in an electric field provided their size is known.

The method described can be further used to obtain unipolarly charged aerosol with a considerable degree of uniformity of the charges, which is hardly attainable by other methods.[7]

Summary.

1. A method for the determination of the rate of charging of floating particles by an ionic current is described. It consists of passing a narrow cloud-jet parallel to the axis of a cylindrical electric precipitator, and measuring the charges acquired by the particles in it.

2. The experiments were made with oil-droplets ranging from 0·5μ to 3μ radius. The size and charge of the droplets were measured by the " oscillation " method. Current densities of about 3 to 10 $\times$ 10^{-9} Å/sq. cm. and times of charging of about 0·01 to 0·02 sec., were used.

3. A good agreement between the mean values of the measured charges and theoretical values calculated neglecting the effects due to diffusion of ions and to mirror-forces, was obtained for the whole range of sizes studied.

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[7] Fuchs und Petrjanoff, *Phys. Chim. Acta of U.S.S.R.*, 1935, **3**, 327.

AN EXACT THEORY OF THE COAGULATION OF SPHERICAL PARTICLES ARISING FROM THERMAL AGITATION.

By W. R. HARPER.

A general theory of coagulation must first deal with its most fundamental aspect—the bringing together of the coagulating particles by thermal agitation. Comparison with experiment is then possible, since this simple mechanism is almost certainly adequate to account for the coagulation of smokes, and appears also to be adequate to account for the coagulation of some colloidal solutions. A theoretical treatment for spherical particles has been given by Smoluchowski,[1] and his results confirmed experimentally by Tuorila, and by Patterson and Cawood. The present author, however, has given reasons for doubting the validity of the interpretation of these experiments, and has shown that the theoretical treatment as presented by Smoluchowski is open to serious criticism, being self-contradictory. The coagulation coefficient was obtained by him by a consideration of the diffusion of particles in a concentration gradient which was itself established by the coagulation process, and which was therefore *not* present previous to the coagulation, *i.e.* not present during the motion which actually determined the rate of coagulation. His treatment might therefore very well give an incorrect value for the coagulation coefficient. Moreover, an alternative treatment of the author's [2] (subsequently corrected [3] for a numerical error) gave a value for the coagulation coefficient which was three-quarters that obtained by Smoluchowski. The mathematical methods employed, however, being approximate, could only suggest, and not prove, that Smoluchowski's result was numerically incorrect.

The possible existence of a considerable discrepancy between theory and experiment at the very basis of coagulation theory was a serious matter demanding further investigation, and it was therefore important to determine the true theoretical value of the coagulation coefficient by a method at the same time both logically rigorous and mathematically exact. It is possible to improve the author's previous treatment so as to conform to these standards, and this will be done in the present paper. The result obtained is identical with that of Smoluchowski.

It might therefore be thought to have been more satisfactory to have attempted a reconsideration of Smoluchowski's own treatment, in the hope of obtaining it in a revised form freed from the objections already mentioned. The author has made such an attempt. Further doubtful steps in the argument were thereby revealed, some being concerned with factors of two. At the same time, it did appear that by presenting the argument in a different form, the coagulation coefficient *could* be made to depend on a calculation similar to that of Smoluchowski's, and probably leading to the same value for the coagulation coefficient. Hitherto,

[1] *Z. physik. Chem.,* 1917, **92,** 129.
[2] *Trans. Faraday Soc.,* 1934, **30,** 636.   [3] *Ibid.,* 1935, **31,** 774.

however, the author has not succeeded in obtaining this argument in a form exempt from criticism, so it will not be given here.

The Collision Problem.

If collision always leads to coagulation, the coagulation coefficient may be written down once the frequency with which particles collide is known. It is irrelevant for the purpose of the present calculation whether the collisions leading to coagulation are collisions with contact, or merely approach to within a certain critical distance. We therefore consider a system of points (the centres of the spherical particles) which move along tracks determined by random collisions with the molecules of the surrounding medium, and therefore by the laws of the Brownian movement, and which are said to be in σ collision when they are within a distance σ apart. They are contained in a volume which is very large compared with the probable path of a particle before it suffers a σ collision, so that the collision frequency is the same as for a distribution of infinite extent. If the particles differ in size, we consider the frequency of collisions of particles of a certain size, characterised by centres with a diffusion coefficient D_1, with particles of another size, characterised by centres with a diffusion coefficient D_2, their concentrations being n_1 and n_2 respectively. This collision frequency will be unaffected by the presence of the other particles if, as will be assumed, the particulate volume is large compared with the volume of a particle (or its sphere of action).

We are dealing with relatively high concentrations, so a large number of collisions can occur before the concentration is appreciably affected, and the collision frequency must be calculated from what happens during such a time. The initial distribution of each set of particles in space is the distribution at any stage of the coagulation, and has been reached by the processes of diffusion and coagulation. The former leads to a random distribution, and the latter does not disturb it. But the distribution of one set of particles about any particle of the other set, averaged over all such particles, is not random, being disturbed by coagulation. This is because some particles of a random distribution are actually in collision, have therefore coagulated, and really belong to a set of particles characterised by another diffusion coefficient. They must therefore not be included in the averaging. This eliminates all particles of the second set which have particles of the first set closer to them than a distance σ between centres. The required distribution of the centres of the first set about those of the second has therefore zero concentration up to a radius σ. The distribution of the particles of the first set about any eliminated particle of the second set is, however, random outside the radius σ, from which it follows that the required distribution of the centres of the first set about those of the second has a uniform concentration n_1 of randomly distributed centres outside the radius σ.

We may take this initial distribution of centres and use appropriate equations of motion to investigate how long it will be on the average before another collision occurs in the system, from which the collision frequency may be deduced. It is this method which leads to mathematics similar to Smoluchowski's, but we shall not pursue it further, since it is not the most direct line of attack. The result obtained by following it through comes entirely from the initial slight deviation from a random distribution, and therefore depends on a logical subtlety,

since it is clear from physical intuition that the deviation is irrelevant in a direct calculation of the collision frequency, which depends on how quickly the centres move about, and on their average distance apart, and not on their *precise* distribution. That the precise initial distribution is not important will now be proved.

In a direct treatment we have to consider each centre of the second set moving among the first set, calculate its probable lifetime before collision, and average over all the second set. This gives the probable lifetime of a centre of the second set, and hence the collision frequency. Now the departure of the initial distribution from a random one affects the average lifetime before collision in that some second set centres of a random distribution are excluded from the averaging, and to these centres belongs a probable lifetime which is shorter than the average for the random distribution. The true average is therefore longer than the average for a random distribution by an amount which is equal to the difference between the average for the actual distribution and the average for the excluded centres multiplied by the fraction of the centres excluded. The former is of the order of magnitude of the true average, and the latter is equal to the fraction of the centres of the second set which are in collision at any time, which is equal to the volume of a sphere of action of the second set divided by the particulate volume for the first set, and this ratio has been postulated to be very small. We shall, therefore, incur a negligible error by calculating the average lifetime on the assumption that the initial distribution is strictly random. This is actually the case for our two sets of centres if the sphere of radius σ is a pure mathematical fiction, so that, on collision, interpenetration instead of coagulation occurs. Again referring to physical intuition, it is clear that the assumption of interpenetration will not affect the collision frequency, since its magnitude depends on how quickly the centres find each other, and not on what happens during a collision. We shall calculate the collision frequency for a system in which interpenetration occurs.

In spite of what has just been said, it is clear that the rate at which centres find each other *is* correlated with the time they remain within a distance σ during an *interpenetrating* collision, and we shall now make use of this correlation. Consider any given large volume V, containing n_1V centres of the first set, each centre being surrounded by a sphere of radius σ. Since the particulate volume is large compared with the volume of such a sphere, the spheres overlap to a negligible extent, and the fraction of the volume V occupied by them is $\frac{4}{3}\pi\sigma^3 n_1 V/V = \frac{4}{3}\pi n_1\sigma^3$. Now the distribution of the centres of the second set is purely random, so if we consider a particular centre of the second set, the chance that it is located in a particular volume inside V at any time is just the ratio of this volume to the total volume V, irrespective of the position or shape of the volume considered. The probability that the centre of the second set is in σ collision with some centre of the first set at any time is therefore $\frac{4}{3}\pi n_1\sigma^3$. Another expression for this probability may be obtained from a consideration of the life history of the centre of the second set during a long time T. During this time, it suffers $\nu_2'T$ collisions, where ν_2' is the collision frequency for a single centre of the second set. If the average duration of a collision is τ' it is in collision for a total time $\nu_2'T\tau'$. The fraction of the time it is in collision is $\nu_2'\tau'$, and this is equal to the probability of finding it in collision at any time. We therefore have $\frac{4}{3}\pi n_1\sigma^3 = \nu_2'\tau'$. The collision frequency ν' for the system is $n_2\nu_2'$, and is therefore $\frac{4}{3}\pi n_1 n_2\sigma^3/$ '

We have now to resolve an ambiguity in the definition of the average duration of a collision. If we consider a centre which comes from infinity to collide with another centre, and then returns to infinity, it is clear that owing to the tortuous nature of its track it will, in general, approach to within a distance σ, and recede to a greater distance several times, thus making a multiple collision. Moreover, the multiplicity will be very high if the mean free path of the centre (between bends in its track) is small compared with σ, as is the case in the present problem. But the probability of return to within the distance σ is only appreciable if the centres have not separated to a distance many times σ, that is, if they have not been likely to have collided with some other centre. When, therefore, the first collision of a multiple collision is sufficient to lead to coagulation, the rest are wasted from that point of view, and the multiple collision counts as a single collision.[4] What we require, therefore, is the collision frequency in the sense of the number of different centres visited per second, and in calculating the value of τ' we must sum up all the individual times spent within the distance σ that refer to the different collisions of a multiple collision.

FIG. 1.—AB and CD are tracks which are not members of the subset. EG and HK are two tracks which are members of the subset, HK being a track showing multiplicity in collision. The contribution of these two tracks to the time average comes from the sections within the sphere of radius σ, i.e. from the sections of track which are thickened. The sections of track FG and JK are typical of tracks starting at F and J respectively.

The Case of $D_2 = 0$.

We shall consider first the case of $D_2 = 0$, so that only particles of the first set move. The procedure for calculating the average duration of a collision then reduces to the following, the details of which will perhaps be understood more clearly on reference to Fig. 1, which is purely schematic. We take a sphere of radius σ whose centre corresponds with the centre of a particle of the second set and is therefore fixed, and a set of tracks characterised by a diffusion coefficient D_1 which start at

[4] The situation is very different if collision does not invariably lead to co-agulation. See Fuchs, *Z. physik. Chem.*, 1934, **171A**, 199.

random at infinity and return to infinity, and we consider the subset of those tracks which pass through the sphere. We add up the total length of track within the sphere, express it as a time, and divide by the number of tracks in the subset, thus obtaining τ'.

Now the subset is chosen from the set in the following manner. Starting at infinity at the beginning of a track, its course is followed. If it returns to infinity without passing through the sphere it is excluded from the subset. If it reaches any point on the surface of the sphere, it is immediately included in the subset. The sections of track in the subset which lead up to the sphere are therefore not typical of Brownian movement tracks starting at the surface of the sphere, since some of the tracks defined in this way would pass through the sphere, and the actual sections of track do not. But assigning a track in the set to the subset in the manner stated does not affect the completely random nature of the track once it is so assigned, so the sections of track in the subset executed after reaching the sphere are typical of Brownian movement tracks starting at the surface of the sphere, and moreover, they include all the track within the sphere. τ' may therefore be calculated as the average time spent within the sphere by centres starting at a point on its surface and moving along Brownian movement tracks to infinity. When adding up the total time spent by the centres within the sphere and dividing by their number, it is irrelevant which centre contributes which element of time, so we may obtain the average from the distribution of the centres given as a function of the time, without having to follow the detailed history of the individual centres. The distribution function required is that for a set of centres starting together from a point at time $t = 0$, and then diffusing outwards, and is well known.

If Q centres start from the point on the surface of the sphere, and at time t there are $q(t)$ within it, then

$$\tau' = \frac{1}{Q}\int_0^\infty q(t)\mathrm{d}t.$$

Now, the number of centres that are situated within a spherical shell defined by r and $r + \mathrm{d}r$ whose centre is the starting-point is

$$\frac{Q}{2\sqrt{\pi}}(D_1 t)^{-\frac{3}{2}} r^2 e^{-\frac{r^2}{4D_1 t}}\mathrm{d}r.$$

The fraction of these inside the sphere of radius σ is equal to $1/4\pi$ times the solid angle subtended by the spherical cap of intersection of the two spheres at the starting-point, and is $\frac{1}{2}\left(1 - \frac{r}{2\sigma}\right)$. The total number inside the sphere is therefore

$$q(t) = \int_0^{2\sigma} \frac{Q}{4\sqrt{\pi}}(D_1 t)^{-\frac{3}{2}} r^2\left(1 - \frac{r}{2\sigma}\right)e^{-\frac{r^2}{4D_1 t}}\mathrm{d}r,$$

and $$\tau' = \frac{1}{4\sqrt{\pi}}\int_0^\infty\int_0^{2\sigma}(D_1 t)^{-\frac{3}{2}} r^2\left(1 - \frac{r}{2\sigma}\right)e^{-\frac{r^2}{4D_1 t}}\mathrm{d}t\mathrm{d}r = \frac{\sigma^2}{3D_1},$$

whence the collision frequency $\nu' = 4\pi n_1 n_2 \sigma D_1$ for $D_2 = 0$, the value obtained by Smoluchowski.

The General Case.

The earlier approximate treatment of the author gave reason to suppose that the collision frequency for both sets of particles moving

could not be obtained from the case of $D_2 = 0$ merely by substituting $D_1 + D_2$ for D_1 in the formula. It will now, however, be shown that an exact treatment *does* lead to this simple result.

In calculating the average duration of a collision, we have now to allow for the motion of the centres of the second set, that is for the motion of the centre of the sphere of radius σ, or what comes to the same thing, for the motion of the starting-point on its surface. The probability of a particular radial displacement of the starting-point is given by a distribution function of the same form as that used for the motion of the centres of the first set, but with D_1 replaced by D_2. τ' will now be given by the same integral as before, but with $q(t)$ appropriately averaged. This must be done by taking the number of centres of the first set which are within the sphere of radius σ when the starting-point has suffered a given displacement, multiplying by the probability of the displacement, and integrating over all possible displacements. A detailed integration has been carried out along these lines, and leads to the conclusion already stated. It will, however, not be given here, since it is lengthy, and since the same conclusion can be reached by the following general argument.

It is clear that the integral for τ' is correctly modified to allow for the motion of the starting-point if instead of expressing it in terms of the probability of a given displacement of a centre of the first set relative to a fixed origin, we use the probability of a given displacement of a centre of the first set relative to a centre of the second. It was proved by Smoluchowski[1] as part of his own treatment that this probability is given by a formula which is the same as the one originally used except for the substitution of $D_1 + D_2$ for D_1. This substitution will lead to the same change in the formula for τ', so the general collision frequency will be $\nu' = 4\pi n_1 n_2 \sigma (D_1 + D_2)$.

Summary and Conclusions.

It has been shown that whereas the criticisms advanced elsewhere by the author against the theoretical treatment of Smoluchowski remain justified, an exact treatment leads to precisely the same formulæ, thus contradicting the indications of the author's previous approximate treatment. It follows that the theory of the effect of heterogeneity given by Smoluchowski requires no modification.

The theory, however, is only applicable to spherical particles coagulating to give spherical particles, and as pointed out in the author's previous paper, a departure from these conditions must lead to a marked change in the coagulation coefficient. The agreement between the calculated rate of coagulation for particles which coalesce on coagulation so as to form new spherical particles, and the observed rate for oleic acid smokes, must now be taken as showing that the different cohesive forces for different orientations of the long chain compound do not have the result of deforming the droplets appreciably from the spherical shape, and that even if an adsorbed surface layer does prevent true coalescence on coagulation, yet the resultant complex droplet is deformed into a shape which is nearly spherical. The further agreement with the observed rate of coagulation of stearic acid smokes must be taken as showing that the stearic acid is a super-cooled liquid in the early stages of the coagulation, even though it is solid in the later stages. It is unfortunate that experimental evidence is not available to check these conclusions directly.

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GENERAL DISCUSSION.*

Professor R. Whytlaw-Gray (*Leeds*) said : Experimental evidence suggests that the rate of coagulation is not greatly influenced by the shape of the particles. The constants for smokes of stearic and oleic acids agree closely with theory whilst that for ferric oxide of the same weight concentration is only 30 per cent. greater. When these smokes are allowed to coagulate until the particles are large enough to be seen with the microscope, the stearic acid complexes, though not truly spherical, are of a compact form, whilst those of ferric oxide are loosely built, chain-like structures, formed of units which appear like beads on curly strings.

The difference in structure of the two types is striking and if the ultra-microscopic particles possess the same form as those of microscopic dimensions, it is surprising that the coagulation constants for the two smokes do not show a greater divergence.

It is therefore evident either that the form of the particles has a relatively small effect on the coagulation rate, or that the ultramicroscopic particles even in a smoke like ferric oxide, with such a marked tendency to chain formation, are spherical in the early stages. Examination by X-ray or electron diffraction methods might enable the size of the units in these aggregates to be estimated and thus throw light on this question.

Mr. W. Barrett (*Gerrard's Cross*) said : In the equation $dn/dt = -Kn^2$, K has the dimensions of (frequency) × (volume). This suggests that there may be a fundamental frequency, but nothing of the kind seems to appear. For purposes of extrapolation it would seem preferable to use the form $dn/dt = -Kn(n - \mathrm{I}/V)$ where V is the volume occupied by the smoke. The integral of this is

$$\frac{\mathrm{I}}{nV} = \mathrm{I} - e^{-\frac{Kt}{V}}$$

which does not, as the classical equation, lead to a value less than unity for the total number of particles at the end of infinite time. The curve is tangential to $\mathrm{I}/n = Kt$ at the origin and asymptotic to $nV = \mathrm{I}$ at infinity.

Professor J. C. Philip (*London*) said : Is it not possible that the gap between the molecular state and that of the " primary particles " is associated with the high curvature of extremely small droplets (particles) and the correspondingly high vapour pressure ?

Mr. A. G. Grant (*communicated*): Dr. Fuchs' paper is the only one in this section applying specifically to electrical precipitation phenomena, and I have endeavoured to compare the authors' results with values obtaining in full scale plant working.

The charging of a particle in an electric field is in effect the collection of electronic charges up to a saturation value determined by the dielectric constant and radius of the particle and the strength of the field. Millikan in his Oil Drop Apparatus has demonstrated that in a feebly ionised field, the rate of electron charge collection is relatively small, and in fact he was able to study the successive addition of small numbers of electrons.

In the more strongly ionised fields obtaining in electrical precipitation, it has generally been assumed that a particle acquires its saturation charge in negligible time, this charge being given by the first half of expression (1) in the authors' paper. The authors have now demonstrated that a measurable time is required to reach saturation in accordance with the correction

applied by the expression $\frac{\cdot}{\mathrm{I}} +$

In their experiments only 30 per cent. of the maximum charge was reached in the measurable time of approximately 0·02 seconds. It is to be regretted that they were not able to make determinations and to plot

* On the three preceding papers.

results for a wider range of times, as their work resolves itself into a single point determination—that is, we now know only that expression (1) is correct for complete saturation when the value of time is relatively great, and for partial saturation at the one time, 0·02 seconds. Nevertheless we can probably assume the validity of the time correction.

Now, whilst in precipitation work, values vary over a wide range, I think we can take, as typical lower values, a field strength of a thousand volts per centimetre, and an ion concentration of 10^8 per c.c. These figures are respectively twice and ten times those used by the authors. We can retain their particle radius of the order μ. Inserting these values in their expression for particle charge, we obtain altogether higher degrees of charging. For times of 0·5 seconds upwards, the departure from saturation is negligible. At 0·05 seconds the degree of saturation is 80 per cent.

In precipitation work, I think we can say that 0·5 seconds is the lower limit for time of contact of a particle in the ionising field. In this time and for values I have just assumed, 97·5 per cent. of the maximum charge is acquired by the particle. It thus appears that the authors' work in establishing the validity of the time correction has enabled us to show that in ordinary precipitation work the time factor can be ignored ; that the earlier assumption, though without justification, that precipitation calculations can be made on the basis of a fully charged particle, was in fact correct.

I think an explanation is easy to find. The velocity of a particle in the electric field varies directly as its charge, so that a 50 per cent. charged particle will be precipitated in double the time required by a fully charged one. Thus time for removal is a function of charge, and charge is a function of time. Now since removal time is large, compared with the required charging time, it automatically follows that a field so designed as to remove the particle, will automatically give it its saturation charge.

This paper is of very great practical value as being, to my knowledge, the first successful attempt to determine the time factor under controlled conditions, and I hope that my remarks will not be taken by the authors to imply that their work has been other than constructive.

Dr. N. Fuchs (*Moscow*) (*communicated*) : I cannot agree with the objections to the theoretical treatment of coagulation given by Smoluchowski which are put forward by Mr. Harper. The deduction of Smoluchowski can be presented in a form which does not require the explicit use of a " concentration gradient," attacked by Mr. Harper, and approaches the treatment given by Mr. Harper himself.

Let $W(x, y, z, t)$ be the probability that a material point with co-ordinates x, y, z, performing the Brownian movement will cross a certain immovable surface at least once during time t. Kholmogoroff [1] showed that W must satisfy the Einstein-Fokker equation

In the case of a spherical surface with radius σ, W depends only on the distance r between the material point and the centre of the sphere, and equation (1) takes the form

From the physical significance of $W(r, t)$ it is clear that $W(\sigma, t) = 1$ when $t > 0$, and $W(r, 0) = 0$ when $r > \sigma$. The solution of (2) is therefore :

$$\frac{\sigma}{r} - \frac{2\sigma}{r\sqrt{\pi}} \int_0$$

[1] Kholmogoroff and Leontowitch, *Physik. Z. Sovjetunion*, 1933, **4**,

We have thus obtained an expression for the probability that a material point (whose distance from the centre of a sphere σ is r) will cross its surface at least once in time t.   If at the moment $t = 0$ the spheres σ are distributed at random with the mean concentration n, there will be $4\pi r^2 n\mathrm{d}r$ of them within a spherical shell defined by r and $r + \mathrm{d}r$, whose centre is the initial position of the material point, and the point will cross in time t the surface of as many as

$$\mathrm{d}I = 4\pi W(r, t)nr^2\mathrm{d}r$$

spheres.

The total number of the spheres crossed will be :

$$I = 4\pi n\int_{\sigma}^{\sim} W(r, t)r^2\mathrm{d}r. \qquad . \qquad . \qquad . \qquad . \qquad (4)$$

In unit time it gives :

and that is exactly the equation obtained by Smoluchowski.   It differs from that deduced by Harper by the factor $1 + \dfrac{\sigma}{\sqrt{\pi D t}}$, which rapidly approaches unity.   The physical significance of this factor is obvious : in our deduction we counted only the spheres crossed by the material point the first time, and did not pay any attention to the subsequent crossings of the same sphere.   At the beginning of the process the point is surrounded by those spheres which it has not yet crossed and, therefore, the number of registered crossings in unit time is larger than later on, when a certain stationary distribution of spheres, which have already been crossed, is established around the point.   In the treatment given by Harper which is based on averaging the time spent by the material point within a single sphere this circumstance is omitted.

The deduction cited above shows that the theory of coagulation given by Smoluchowski is correct in all cases where equation (1) is valid, *i.e.* when the radius of the particles is large in comparison with their " apparent mean free path." [2]   If this condition is not satisfied, a correction for the " concentration drop " at the surface of the spheres σ, diminishing the rate of coagulation, must be introduced in the equation (5).   This drop is quite similar to the well-known temperature-drop and velocity-drop (slip) at the surface of small spheres in gaseous media, and was taken into account for the first time by Townsend [3] in his theory of diffusion of ions towards small conducting spheres.   For particles of 10^{-5} cm. radius this correction makes a difference of only few per cent., but for 10^{-6} cm. particles it is already very considerable. [4]

In reply to Mr. Grant (*communicated*) : I must emphasise, that our work is substantially a further development of the excellent work of M. Pauthenier and co-workers cited in our paper.

The chief result obtained in our laboratory is that the charging-equation derived and experimentally tested by Pauthenier over a wide range of time remains exactly valid for small particles.   Although this result was obtained for a small range of time (0·01–0·02 sec.) only, there remains little doubt as to its applicability over the whole range of the charging.

On the other hand it seems that the applicability of Pauthenier's equation to small particles ($\sim 1\mu$) is limited to comparatively large values of the field-strength as used in electric precipitators.   In a weak field the effect due to the diffusion of ions can by no means be neglected.

[2] Smoluchowski, *Annal. Physik.*, 1906, **21**, 769.

[3] Townsend, *Electricity in Gases*, Chapter 6, 1915.

[4] Fuchs, *Z. physik. Chem.*, 1934, **171**, 199.

Dr. W. R. Harper (*Bristol*), in reply (*communicated*) : I may appear to be excessively insistent on mathematical rigour, but there is good reason for it. In developing my own treatment a certain step in the argument seemed mathematically obvious not merely to myself but to others whom I consulted. Moreover there was a proof to justify it. Nevertheless it subsequently appeared that the proof was faulty and that what had seemed obvious required changing by a factor of two. I conclude that the result of any treatment is only to be trusted when obtained by flawless reasoning.

Doubts of this nature concerning the treatment of Dr. Fuchs restrained me from taking the initiative in discussing it, but I would now say that his treatment seems to me to be perfectly rigid with one proviso and one exception. The proviso is that the treatment be presented as a calculation of the collision frequency in a system of interpenetrating spheres as in my own treatment, and subsequently applied to the actual coagulation problem with the justification therein given. We can then choose one centre out of the system and follow its track from $t = 0$ to $t = \infty$, calculating how many spheres it intersects per second, and avoid having to picture it as possessing the incompatible properties of being able to collide with a number of spheres without changing its identity, and becoming a different particle after each collision. It is ensured that multiple collisions are counted as single by working with the probability that each surface is crossed at least once, and by neglecting the initial part of the solution. A comparison of the initial form with the ultimate form of the solution now shows that the multiplicity of a collision must be infinite, it being presupposed however that the mean free path of the centre is infinitesimally small, its track velocity being of course infinite to give a finite diffusion coefficient.

The apparently innocent assumption that $W(\sigma, t) = 1$ for $t > 0$ appears to me to require proof, and this is not given in the work of Kholmogoroff referred to. For it to be correct, a centre starting infinitely near a plane surface cannot move to a finite distance from the surface without crossing it at least once, and it would seem pre-supposed that the mean free path is to be taken as an infinitesimal of the second order, since we are considering Brownian motion and not a phenomenon dependent on track velocity. We may magnify the picture and conclude that the assumption is only correct if a centre starting at a finite distance from an infinite plane surface and executing Brownian motion with an infinitesimally small mean free path cannot move to infinity without crossing the surface. Whether or not this is so, seems to me to be by no means obvious, but it must be so since Dr. Fuchs and I obtain the same value for the coagulation coefficient.

I cannot admit that the treatment of Dr. Fuchs disposes of my objections to the treatment of Smoluchowski—I would say rather that it avoids them. It is difficult to decide from the original papers of Smoluchowski just what significance he intended to be attached to his mathematics, but from the formulation in the *Zeitschrift für Physikalische Chemie*, it seems clear that the colloid particle is to be regarded as analogous to a large sphere on which particles of vapour are being condensed, in which case the objection that the colloid particle has coagulated before even the establishment of the boundary conditions which lead to the solution of the problem for the large sphere can be made precise, and is surely valid. I now see however that this objection and others can most simply be met by again presenting the mathematics as a derivation of the collision frequency for a system of interpenetrating spheres and then applying the result to coagulation with the appropriate justification, instead of presenting it as a direct calculation of the rate of coagulation. We choose one sphere out of the system at time $t = 0$, and calculate for all subsequent time how many centres cross its surface per second for the first time. This clearly gives the collision frequency for the sphere if multiple collisions are counted as single collisions, except that the initial part of the solution must again be neglected because we are then counting some collisions which really belong to

time previous to $t = 0$. Smoluchowski's method of calculating the number of first arrivals is of course to solve the diffusion equation with the appropriate initial conditions and the boundary condition of zero concentration. He justifies this on the ground that it works for the particular case of a plane surface, from which one may conclude that he regarded it as plausible but unproven that it is correct in the general case. It may however be proved in the following way : Consider any initial distribution of centres in space situated on one side of any closed surface. It is required to find the mean number of centres that will have crossed the surface at least once in time t. This is equal to the number that would have been removed from the distribution if the surface annihilated them on arrival. The annihilation may be carried out by creating a negative centre when and where a (positive) centre arrives at the surface, but otherwise allowing both sets of centres to diffuse unimpeded by the surface. The distribution of both positive and negative centres is governed by the diffusion equation, so the actual distribution of centres (with annihilation at the surface), being the difference between these distributions, is also a solution of the diffusion equation. That it is the solution with concentration at the surface put equal to zero follows from the fact that if it were not, there would be maintained a concentration discontinuity at the surface (the concentration inside being ex hypothesi zero), which would result in an infinite rate of removal of centres from the distribution, and this could not be maintained.

The treatment of Smoluchowski can therefore be presented in a mathematically rigorous form leading to the usual result. It can, moreover, be transformed into my own formulation, thus providing a cross check. We may therefore conclude that there is now no doubt whatsoever about the value of the coagulation coefficient.

INTRODUCTORY PAPER, PART I.(b) THE GENERAL PROPERTIES AND BEHAVIOUR OF DISPERSE SYSTEMS CONSISTING OF AQUEOUS AND OTHER VOLATILE PARTICLES, i.e. MIST, CLOUD, HYGROSCOPIC NUCLEI, TOWN AND COUNTRY FOGS.

By G. M. B. Dobson.

Received 13th March, 1936.

Meteorological Aspects.

I have been asked by the Council to give a short introductory talk on the meteorological aspects of Dust, Smoke, and Fog. I think that it will be best if I try to give a very brief résumé of our knowledge of this subject at the present time, and thereby to reveal where our ignorance is greatest and where more work is particularly wanted.

With regard to atmospheric haze and fog—whether in country or town—the main physical principles appear to be known, but there is much that requires further elucidation. In clear air, free from fog, there are always present a large number of minute particles, some of which are hygroscopic, while others are not so. In country districts, particularly near the sea, the hygroscopic particles may be largely sea salt derived from sea spray, while in towns, those due to combustion of fuel, such as droplets of H_2SO_4, will probably outnumber the others.

It has been suggested that nuclei are formed by sunlight, but this does not seem to be certain.

These hygroscopic particles will condense upon themselves an amount of water depending on the relative humidity of the surrounding air, until they are in equilibrium and their vapour pressure is equal to that in the air. Their size will thus vary with the relative humidity, while their number remains constant. Thus the visibility will depend on the relative humidity as was shown by Aitken. On the other hand, the non-hygroscopic particles will remain constant in size and add an amount to the haziness which is independent of relative humidity.

Many of these minute particles can be seen in the ultra-microscope (possibly all, if the illumination be good enough), and if arrangements be made to saturate the air and cool it by a slight expansion, the condensation of water upon them is immediately seen. The particles are clearly of all sizes, and so far as I have seen, most of them seem to have water condensed on them at a supersaturation of 1 or 2 per cent. forming droplets. An estimate of the size of individual particles can be made from the magnitude of their Brownian motion. The particles appear to have a radius of a few times 10^{-6} cm. The smaller particles therefore scatter light to an extent which depends on the inverse fourth power of the wave-length of the light and on the sixth power of the radius of the scattering particle. (Owing to this sixth power law, the smallest particles are very difficult to see in the ultra-microscope and, judging by the brightness, the particles appear to vary in size more than they really do.) On the other hand, the larger particles scatter all wavelengths alike, hence the increasing whiteness of the sky in hazy conditions.

When the humidity approaches saturation, a large amount of water will condense on the hygroscopic particles, their equilibrium being governed by the opposing effects of surface tension and osmotic pressure. If these two alone determine the size of the drop, it must pass through an unstable size, and as the relative humidity increases, it would slowly grow, and at some point suddenly jump to a much bigger diameter. There are, however, two other things of which we must take account, firstly the removal of water vapour from the air by condensation on the drop, and secondly the effect of latent heat of water. It can be shown that if the initial hygroscopic particles are sufficiently large and numerous, the effect of the removal of water vapour may prevent any unstable growth, while the effect of the latent heat set free, must tend to prevent any sudden condensation.

That only a small number of the original nuclei grow into fog droplets during a fog, is easily seen in the ultramicroscope, where the relatively large fog droplets are seen like brilliant stars falling across the field of view, and at the same time a far larger number of the minute particles are seen, such as are present when there is no fog. This, of course, is what theory would lead us to expect, as the largest hygroscopic particles would first grow into fog droplets, and, only after these were removed, would the smaller particles increase greatly in size. This should make us reflect whether we are making the best observations for meteorological purposes if we measure the total number of hygroscopic particles present in the air as we do with the Aitken Counter. Should we get a more useful measure for meteorological purposes' if we counted only the number of particles which condensed water sufficiently easily to form nuclei for fog and rain drops ?. This number is probably much smaller than the number counted by the Aitken apparatus. The difficulty

would be that there are probably particles of all types present in any sample of air, forming a continuous series, and we should have to draw some arbitrary line between those that readily act as condensation centres, and those which require some considerable supersaturation.

It is clear that the relative humidity must be approximately 100 per cent. in a fog, but it is not certain whether it may be a little above or below this value. From the effect of surface tension we should expect it to be slightly above 100 per cent. but it seems possible that the droplets and nuclei may be cooled by radiations slightly below the temperature of the surrounding air, so that they will be in equilibrium at a relative humidity slightly below 100 per cent.

The processes taking place after the fog has formed, are not entirely clear. If the hygroscopic nuclei are of such a size that there is an unstable period in their growth, and if cooling continues slowly in air already at 100 per cent. R.H., one would expect the excess water vapour to condense out on the existing droplets, so that these would increase in size, but there would be little increase in the number of droplets, unless those initially formed had fallen out of the air. On the other hand, if the hygroscopic nuclei are so large and numerous that there is no unstable period in their growth, the larger ones might become stable, and condensation occur on those slightly smaller. Which of these represents the facts in nature I do not know, possibly one in clean country air, and the other in towns. Certainly as a fog gets thicker, the number of droplets appears to increase.

It has been stated that the sizes of fog droplets fall into definite groups, so that those of one group may be explained as due to the combination of two drops of a group with smaller size. Again measurements have been given showing that while drops of all sizes within a wide range are present in any fog, there is in any given fog a particular radius which is most common, and that this radius is always a whole multiple of a certain value. Before the meteorological world will accept any of these views, they will clearly require many more observations.

The fog droplets being of the order of a few microns in radius, scatter all wave-lengths of light alike, hence the sun seen through a country fog appears white, and it is only in a town fog where there may be a large number of minute particles in addition to the water droplets, that the sun may appear red in a fog. This shows that the benefit to be expected from coloured lights when driving in a fog is negligible.

It seems probable that electrical conditions have no appreciable effect on the equilibrium of fog particles. That mobile ions are caught on the fog droplets is well known, the conductivity of the air thereby being greatly reduced, causing the great increase in the electric potential gradient usually observed in a fog.

The conditions when a fog evaporates, will be largely the reverse of those when it forms, except for two things. Firstly as we have already said, the temperature of the particle may not be exactly that of the surrounding air, and secondly, in towns, the solution of SO_2 in the fog droplets and its slow oxidation into SO_3 may lead to the evaporating droplet being a dilute solution of H_2SO_4 when the droplet will be stable at a lower relative humidity than that at which it was formed. There seem to be few observations to guide us here.

I would call the attention of workers in this field to the value of observations made with ultra-microscopic methods. These may be made either in small glass cells as described by Professor Whytelaw-Gray or,

for use in the free air, they may be much larger. It is quite possible to arrange an intense beam of light with suitable diaphragms, so that the light scattered from the beam by pure dust-free air can be seen. In such an apparatus the small particles present in non-foggy air are seen and their rate of growth with increasing relative humidity can be studied. The advent of the new high pressure mercury vapour lamp shortly to be placed on the market, should make the ultra-microscopic method of much greater value still. A great advantage of the ultra-microscopic method is that the particles and droplets are studied with the minimum of alteration from their natural conditions, and each particle can be dealt with separately, without making any assumption that all particles are alike.

Passing to the removal of particulate matter from the atmosphere, presumably washing out by rain, plays a large part, but our knowledge is very scanty indeed. For instance, is the removal due to the washing action of rain as it falls through the atmosphere or is most of the particulate matter brought down by rain caught at the moment of condensation within the cloud?

We are equally ignorant about the distribution of particulate matter. Thus, how does the pollution produced by a town fall off with distance from the town, under different conditions?

Finally, what is the effect of particulate matter in the atmosphere in cutting off sunlight and daylight? Particularly what is its effect within large cities? Is the decrease of light approximately the same for all wave-lengths, or are there sufficient very small particles in city air to make the reduction of the short wave-lengths much greater than that of the long wave-lengths? Measurements have shown that ultra-violet light may be reduced at the centre of a town, to half the intensity of that received in the suburbs, but such measurements are unfortunately few, and these frequently refer to one band of wave-lengths only.

The discussion of these matters now to take place, is certain to be of great interest, and I hope, will act as a stimulus to still further work on the subject, which is really one of extraordinary importance to the community as a whole.

Oxford.

THE NUCLEUS IN AND THE GROWTH OF HYGROSCOPIC DROPLETS.

By Hilding Köhler (*Uppsala*).

The nature of the nuclei of which a cloud is really formed can best be investigated through the droplets of which the cloud is composed. Such an investigation generally presents great difficulty. After long microscopic investigations I proved that the ice which, in fog, is deposited on mountains as frost is formed through the undercooling of water droplets. The difficulties have thus been reduced to an analysis of such masses of ice.

Since the investigations of Melander and Lüdeling it has been sup-

posed that sea-salts can serve as nuclei of cloud condensation ; that this must be the case has recently been proved by J. H. Coste and H. L. Wright.

From 1919 to 1923 (independently of earlier suppositions) I carried out (on the Haldde) analyses of hoar-frost for chlorine content, on the supposition that sea salts were nuclei of cloud condensation, and at the same time measured the size of the droplets in the fog from which it was deposited.

A. Chlorine.—Generally about 2 kg. of hoar-frost, collected with precautions against contamination, were evaporated to 100 c.c., and the chlorine content determined by Mohr's method of titration.

B. The size of the droplets in fogs or clouds was measured optically. A projector with an arc-lamp and a parabolic mirror sent parallel rays to the observer 61·8 m. away.   The coronæ in the space-grating formed by the droplets were measured.   From the radius of these coronæ the radii of the droplets were measured according to the well-known formulæ :—

$$r = \frac{1 \cdot 220 \, . \, \lambda}{2 \sin \theta_1} ; \quad r = \frac{2 \cdot 233 \, . \, \lambda}{2 \sin \theta_2} ; \quad r = \frac{3 \cdot 238 \, . \, \lambda}{2 \sin \theta_3} ,$$

where θ is the angular radius of the first (θ_1), second (θ_2) and third (θ_3) coronæ, measured at the outer line of the violet colours, and λ is the so-called " wave-length of white light " ($0 \cdot 571 \mu$).   The clearness of the coronæ depends on the homogeneity of the cloud.   If a certain size of droplets sufficiently outnumbers all others we get measurable coronæ.   The more homogeneous the cloud, the clearer are the coronæ, the more distinct the limits ; with a preponderance of drops of a certain size very distinct limits are observed.

Lichen spores were used to give frequency curves of different standard degrees of deviation grouped around an average size.   Measurements of the coronæ given by these spore clouds showed that the spores had dimensions which corresponded with a great accuracy with the average values microscopically measured.[1]   If the standard deviation was great (as for instance in the case of purchased Lycopodium spores), the coronæ became pale and indistinct, since the white colour is dispersed over the different colours, although even in this case the measurements of coronæ gave the size of those spores which are present in the greatest quantity.

By measurements of coronæ in fogs there is thus obtained, the size of those droplets which are in the majority within the field of observation.   If very dissimilar droplets are present to the same extent the coronæ become very indistinct ; according to my experience this is often the case with lowland fogs, and sometimes occurs also in clouds and mountain fogs.   No coronæ at all may arise, if the fog is sufficiently inhomogeneous and no one size preponderates.   A single well-performed measurement of coronæ gives a more reliable value than several millions of measurements of separate droplets.

Results.

1. The most commonly occurring chlorine content was about 3·5 mgm. per litre of melted ice.   It is very remarkable that other concentrations could, within the limits of error, be written $3 \cdot 595 \times 2^p$, where p is a whole number, positive or negative.   The highest and lowest concentrations were 56·33 and about 0·067 mgm. per litre respectively ; although the latter value is uncertain on account of the large experimental errors (amounting

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[1] Hilding Köhler, *Über die Chlorverteilung und die Tropfengruppen im Nebel und über Farbenberechnung der Kränze im weissen Lichte nebst einigen kritischen Bemerkungen der Koagulationstheorien der Nebeltropfen, Arkiv för Matematik, Astronomi och Fysik, K. Svenska Vetenskapsakademien*, **24A**, No. 9.

to 50 per cent.) at such low concentrations. On the presumption that all sea salts are present we get the concentration of these salts per litre of melted ice (according to Knudsen) on multiplication by 1·805.

H. Israël [2] has found almost the same proportion of chlorine in rain, viz., 3·42 mgm., and, thus, 3·42 × 2². The fact that the *concentration* of chlorine in rain-drops diverges only very slightly from the concentration of the droplets in fogs and clouds, the mass of which is about a million times smaller, is of great importance.

Analyses of chlorine content in rain-water carried out over the period 1870-86 by Kinch,[3] gave the following results :—

<div style="text-align:center">

Average of 16 years, 3·81 mgm. per litre.
    ,,   ,, 12 ,,   3·36 mgm. per litre.

</div>

There is therefore no essential difference between the concentration of chlorine in the rain-drops and in the fogs on the level of the Haldde.

On the other hand, my own analyses on the Sonnblick, and similar analyses by Lipp and Lauscher on the Zugspitze and the Sonnblick,[4] have shown that the concentration of chlorine in fogs decreases with the height. Rain generally falls from clouds lying at about the level of the Haldde (914 metres above sea-level). We shall explain later the reason of this decrease of the concentration of chlorine with the height above sea-level.

2. The measurements of the droplets gave an average size of $r = 8·86\mu$. According to theoretical investigations,[1] supported by the experimental observations of L. F. Richardson,[5] a systematic error of, at most, 4 per cent. may attach to this value. Sometimes the size of the droplets changed unduly during a series of measures, and frequently the average value varied from series to series. When frequency curves were drawn for the series of measurements there were always, however, maxima at certain droplet sizes. The relation between those radii which gave these maxima could be expressed as $r = B . 2^{n/3}\mu$ ($B = 8·82$), where n had whole (either, positive or negative) values. I therefore, for all separate measurements, calculated n also. This value (8·82) of B was obtained direct from the frequency curves. Frequency curves of n were drawn for all the measured series and from these it was clear that there is only one maximum, so long as the standard deviation of n is less than or equal to 0·19. With few exceptions these maxima were in the neighbourhood of values of whole numbers of n (or more exactly $n + 0·019 \pm 0·0050$). There further appeared such single series as $n + 0·426 \pm 0·0134$. Frequency curves with a greater standard deviation always showed maxima close to these values of n, although the radii of the droplets often varied from 3 μ to 25 μ.

I therefore made statistical examination, partly to examine the reality of these maxima, and partly to calculate more exactly the values of n. *Thus this work was not carried out in order to prove any particular hypothesis. I have never made any hypothesis of the size distribution of the droplets.* The separate measurements in the single series ($\sigma < 0·19$) grouped themselves round the average values of the whole numbers of n (or $n + 0·445 \pm 0·0070$) according to normal curves with $\sigma = 0·173$. This standard deviation is greater than that of the errors of measurement, which is on an average $\sigma = 0·053$ ($\sigma = 0·131$ for $n = 6$, to 0·029 for $n = -5$).

Hence it follows that the size of droplets present in preponderating proportions in the clouds changes, and that other sizes are found than those which give the maximal frequency.

Series including 2 to 4 maxima were also statistically worked out, and it was found that even these gave normal curves. We then calculated A_3 (the measurements grouped round the whole n, which we now call the

[2] *Bioklimatische Beiblätter*, Heft. 2, 1934.

[3] *J. Chem. Soc.*, 1887, 92.

[4] *Jahresberichte der Sonnblickvereins*, 1931 and 1933.

[5] "The Brown Corona and the Diameter of Particles," *Quart. J. Roy. Meteor Soc.*, 1925, **51**, 1.

3-group), and A_2 (the measurements round $n + 0.445$, which we now call the 2-group). The figures for n and σ and the relative number A, expressed as a percentage of the number of measurements, were :—

	The 3-group.	*The 2-group.*
n :	$n + 0.018 \pm 0.0053$	$n + 0.452 \pm 0.0081$
A :	62.7 per cent.	37.3 per cent.
σ :	0.177 for both groups.	

From all these measurements (which contained series with up to 15 maxima), we calculated by another method the percentage distribution, *viz.* :—

The 3-group.	*The 2-group.*
60.4 per cent.	39.6 per cent.

The distribution of the series earlier calculated being :—

The 3-group.	*The 2-group.*
61.9 per cent.	38.1 per cent.

The two being in unexpectedly good accordance.

If the masses of the droplets was then calculated, it was found that these could be written in the proportions $2 : 3 : 4 : 6 : 8 : 12 : 16$ and so on.

In this mass series, 2×2^n corresponds to the droplets in the 2-group and 3×2^n to the droplets in the 3-group. It has later been found that two other groups probably exist, corresponding to the figures 5 and 7 in the above-mentioned mass-series. The complete series can, then, be written : $2 : 3 : 4 : 5 : 6 : 7 : 8 : 10 : 12 : 14 : 16$ and so on.

These results are empirical and valid for mountain fogs and clouds ; if they are wrong there must be some unknown error in the method of measurement. Recently Niederdorfer [6] has found in rain, by quite another method, the same mass distribution as is given in the above-mentioned series. The results obtained by Findeisen [7] and Hageman [8] are valid for lowland fogs and are obtained through measurements of separate droplets. This method of measurement, which (in regard to droplets in fogs and clouds) has been previously compared with the optical method of measurement, cannot be compared in regard to reliability.

I cannot yet offer any explanation of the classification of the groups of droplets and quantity of chlorine. It has, however, been necessary to give an account of these facts in order to make this description comprehensible.

The Thermodynamics of the Condensation on Hygroscopic Nuclei.

Taking the average values of 3.595 mgm./l. chlorine and radius of droplets 8.86 μ, we proceed, as in a previous paper, [9] where r was taken as 8.82 μ. On the supposition that all sea-salts are present in the nucleus, it is calculated that a nucleus of dry sea-salts has the mass of 1.847×10^{-14} gm. I here take 10^{-14} gm. as mass unit and make $\alpha_1{}^3 = 1.847$. As the quantities of chlorine in the frost are distributed in the proportion 2^p, the masses of the nuclei must also stand in the same relation.

Instead of r I here use n as a variable which varies continually. If $8.82 \, \mu = 8.82 \times 10^{-4}$ cm. $= B$, we then get $r = B \cdot 2^{n/3}$.

[6] *Met. Z.*, 1932, **49**, 1.   [7] *Gerl. Beitr.*, 1932, **35**.   [8] *Ibid.*, 1936, **46**.
[9] Hilding Köhler, *Zur Thermodynamik der Kondensation an hygroskopischen Kernen und Bemerkungen über Zusammenfliessen der Tropfen, Meddelande från Statens Meteorologisk-Hydrografiska Anstalt*, **3**, No. 8, Stockholm, 1926.

From this it follows that $p - n = L$ determines the concentration of the droplet. At a certain value of L the concentration is invariably independent of p and n. Table I gives concentrations expressed in gm. of salt per 1000 gm. of solution at different values of L.

TABLE I.

$p-n=L$.	Concentration gm. per 1.000 gm.
17	529.3
16	326.3
15	184.6
14	98.8
13	51.2
12	26.1
11	13.2
10	6.61
9	3.31
8	1.66
7	0.831
6	
5	Then
4	halve
3	
2	

The total quantity of water in a liquid state in the weight unit of air depends, not only on the concentration of the droplets, but also on the number of nuclei, if every nucleus becomes the centre of a droplet. This number N is of great importance for the understanding of atmospheric condensations.

We now calculate, in terms of the whole quantity of salt being NaCl (since the chemical constants of this salt are well known), and on the supposition that the same laws apply to the small volumes, with which we are dealing, as apply for larger volumes. Now, a salt in water lowers the vapour-tension, but the latter is higher above a convex than above a plane surface. The specific volume v' of a droplet with the radius $B \cdot 2^{n/3}$ and with salt nucleus can be written

$$v' =$$

where δ^3 is a constant, equal to 2.483×10^{-6}. If NaCl has a constant dissociation of 75 per cent., the vapour tension e_l above a plane solution surface can be expressed as :—

$$- \epsilon_a$$

where $\epsilon_a = 9.930 \times 10^{-7}$, $\epsilon_l = 1.149 \times 10^{-6}$, and e_m the pressure of a saturated vapour.

The vapour tension above a droplet of radius $r = B \cdot 2^{n/3}$ of this solution is :

$$2 \cdot s \cdot v'$$

where R_1 is equal to the gas constant of the water-vapour (4706.91),
T is the absolute temperature, and
s is the capillarity constant, which is a function of temperature and concentration as follows :—

$$s = s_0(1 - bT) \cdot \quad 1 -$$

where $s_0 = 1.1683 \times 10^{-1}$,
$b = 1.2518 \times 10^{-3}$,
$c = 8.4 \times 10^{-8}$,
$\beta^3 = 9.960 \times 10^{-7}$.

In order that a droplet of solution shall remain unchanged in the atmosphere, the vapour tension above it must be equal to the pressure of the vapour in the atmosphere. In Fig. 1 the vapour tension above

droplets at different values of α^3 at different concentrations is shown for $T = 273$. It will be seen that the vapour tension first increases with decreasing concentration, passes a maximum and approaches asymptotically the pressure of the saturated vapour. The maxima of the vapour tension become more and more pronounced the smaller α^3 is. If many unequally large nuclei appear in the atmosphere, it follows that on condensation a selection must take place so that, at first, droplets which have been formed on the larger nuclei pass maxima, at which moment droplets on smaller nuclei must evaporate until their vapour tension balances those droplets which have been formed on the larger nuclei. This theoretical result corresponds wholly to the fact that the concentration of Cl in the droplets decreases with the height, as shown by Lauscher and Lipp.[4]

If the sum of the vapour and water absorbed by the hygroscopic nucleus is K, the solution droplets must have a vapour tension equal to the vapour pressure prevailing in the air ; the quantity of vapour x is calculated from
$$x = K - M \cdot 2^n(1 + \alpha_1^3 \cdot \delta^3 \cdot 2^{-pn}),$$
where
$$M = N \cdot \tfrac{4}{3} \cdot \pi(8 \cdot 82)^3 \times 10^{-12}$$
and N = the number of droplets in 1 gm. of air condensed on the nucleus, $\alpha_1^3 \cdot 2^p$ and δ^3 have the same values as before. N is very large ; the larger it is the more quickly x approaches zero.

The latent heat of condensation λ for the solution droplets can easily be calculated :

where A is Joule's equivalent. The middle term in the brackets can be neglected in comparison with the others. From Clapeyron's formula for the latent heat of evaporation of water,
$$\lambda_0 = A \cdot R_1 T^2 \frac{\delta \log e}{\delta T},$$
we get :—
$$. A \cdot T^2 \cdot v' \quad \delta \ / s \backslash \qquad . \quad \_ \quad \_ \quad \delta \, 1$$

In this expression the second term is always negative. The third term is negative, if e increases with decreasing x, which is the case before the maximum of vapour tension has been reached (see Fig. 1) ; this term is greater than the second, so that within this interval
$$\lambda > \lambda_0.$$
After the maximum has been reached, the third term is positive but, since the second term is always negative, it follows that within this interval
$$\lambda < \lambda_0.$$
Without detailing the calculations we can now see how far the droplets increase on nuclei (which we regard as droplets of a more or less concentrated solution of salt) if a quantity of air is adiabatically cooled.

If a quantity of heat q is added to the system of droplets-water-vapour, this heat is used partly in heating the system and partly in evaporation of droplets, according to the formula
$$q = C \mathrm{d}T + \lambda \mathrm{d}x.$$

When the entropy is a whole differential we get

where $F(T) = K$ or the whole quantity of water of the system, so long as the specific heat of water is regarded as independent of the temperature and equal to unity.

We write the change of entropy

$$\int \frac{q}{T} = \int \frac{C}{T} dT + \int \frac{\lambda}{T} dx + const. = S(nT) + const.$$
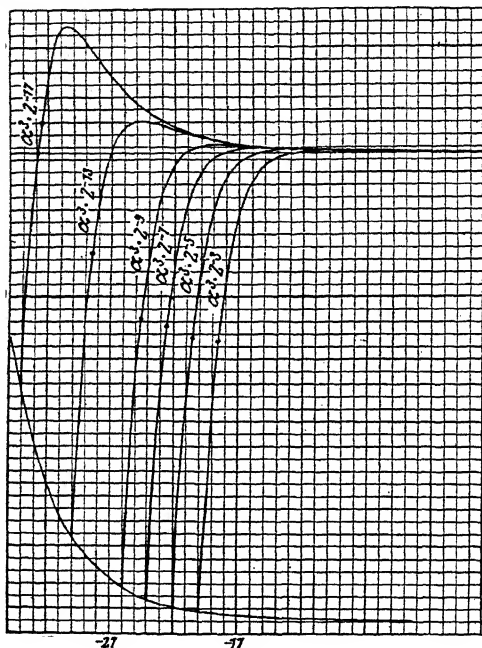
If these processes take place in the atmosphere, the corresponding expression for the changes in the air must be added to this equation :—

$$= c_p \log T - AR \log (P - e) + const.$$

where P = total atmosphere pressure and c_p = specific heat of dry air at constant pressure.

Treating the laws of Boyle-Mariotte-Gay Lussacs as valid for both water-vapour and air we get, if the specific volume of the air is v_1 :—

$$P = \frac{RT}{v_1} - e ; \quad e = x . \frac{R_1 T}{v_1}$$

from which it follows :—

$$\log (P - e) = \log \frac{R}{R_1} + \log e - \log x.$$

Through the setting-up and combination of the two systems we get finally :—

$$\int \frac{q}{T} = S(nT) + c_p \log T - AR \log e - AR \log \frac{R}{R_1} - AR \log x +$$

where e is both the partial pressure of water-vapour in the air and the vapour tension of the droplets. The variation of e_m with temperature is obtained according to the formula :—

$$e_m = 60.49228 - \frac{7027.20766}{T} - 5.8691014 \log T.$$

If the system works under adiabatic conditions $\int \frac{q}{T} = 0$. The constant is determined by the initial conditions. The value of N, which states the number of particles per gm. of dry air is of great importance to the calculations, as also is the choice of α^3. We have chosen N in the following way : N_1 is the number of particles if $\alpha^3 = \alpha_1^3$. Then, $N = N_1 \times 2^p$ if $\alpha^3 = \alpha_1^3 \times 2^{-p}$ and $N_1 = 2 \times 10^5$ corresponds to 258·6 nuclei per c.c. of air, a very small number which may be increased a hundred or a thousand-fold. The first fundamental question may be formulated as follows: Why is the number of droplets in fogs so much smaller than the number often measured with Aitkens' Nucleus Counter?
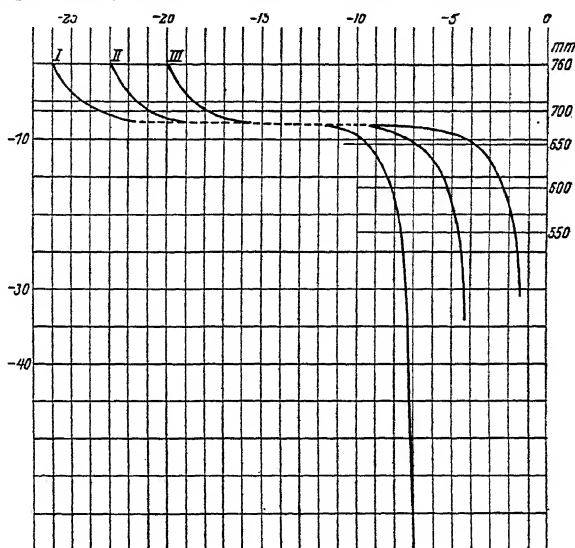
Fig. 2.

I : $a^3 = \iota$ $N = 10^5 . 2^{10}$ per gm. of air
II : $a^3 = \iota$ $N = 10^5 . 2^7$,, ,, ,, ,,
III : $a^3 = \iota$

Fig. 2 shows how the droplets increase (assuming continued condensation) if the initial concentration is expressed by $p - n = 17$, and N has the values shown, the initial temperature being 273 and $P - e$ being initially 760 mm. The first part of the curve is uncertain as not all the NaCl is dissolved until at about $p - n = 15\cdot3$. Thus for $p = -3$, $n = -18\cdot3$. The increase is shown in Fig. 3 for the initial temperature $T = 283$. In both figures n is abscissa and $T - 273$ ordinate, and the atmospheric pressures are also shown.

It will be seen that the increase occurs very rapidly after that the maximal *vapour-pressure* has been reached. Further, the size of droplets at a certain temperature decreases with N. We cannot see so clearly that, after having reached a certain size, the size of the droplets can

no longer be doubled through continued condensation. We have referred to the last value of n, which is obtained through continued condensation as " the last whole n." This value varies with N. The greater N is, the smaller the whole n becomes.
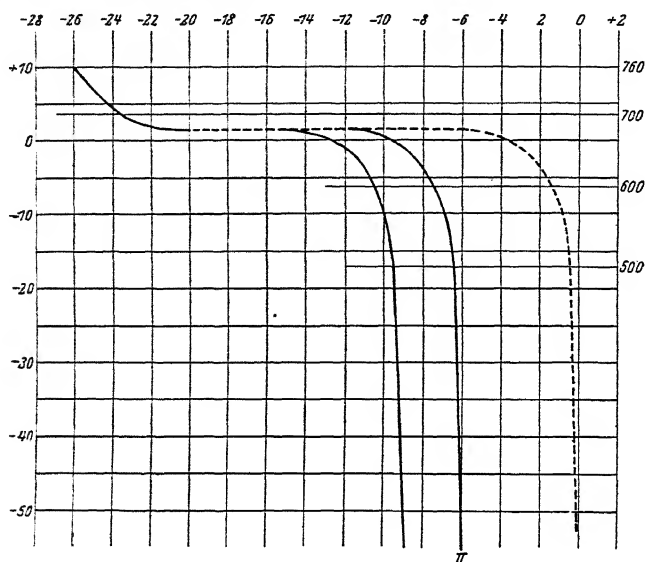
FIG. 3.

I: $N = 8 \cdot 10^8$ II: $N = 10^8$ III: $N = 10^8 \cdot 2^{-6}$ per gm. of air.

TABLE II.

							$+1$	1·798	253·7
							-1	7·190	253·7
16						1·798	253·9	-2	8	253·7
64						7·190	253·9		
128				1·798	254·2	14·38	253·9		
512				7·190	254·2			
1024	- 7	0·899	211·0	14·38	254·2			
4096	- 9	3·595	211·0					
8192	-10	7·190	211·0					

In Table II are expressed the values of the last whole n, the concentration of chlorine in these droplets and the temperature T which this n reaches if the initial temperature is 273 and the initial concentration can be expressed by $p - n = 17$. From this table it follows :—

1. If $\alpha^3 = \alpha_1{}^3$ the droplets can, through condensation, change to $n = + 1$, corresponding to $r = 11 \cdot 11\ \mu$ if the number of nuclei N per gm. of dry air is 2×10^5, corresponding to the low number of 258 per c.c. of air at $0°$ and 760 mm. Through want of vapour the mass of the droplet cannot later on be doubled. If the number of nuclei is 16×10^5 per gm. of dry air or 1064 per c.c., the last whole n cannot on the same nucleus exceed $- 2$, corresponding to $r = 5 \cdot 56\ \mu$. On increasing N the greatest whole n decreases, as is seen, to very small figures.

2. *The concentration of chlorine at these last whole n is that which has in fact been obtained on analysis of hoar-frost.*

3. The greater N is, the more the air must be cooled before the last whole n is reached, the higher the air thus must rise, before this n is reached; thus the concentrations of chlorine due to condensation we have found are reached.

4. The greater N is, the higher the concentration of chlorine is, when the last whole n is reached. At a certain value of N the concentration decreases with α^3, but the last whole n remains the same for different α^3, as long as N is the same. If the initial temperature T is 283, the last whole n is only one unit greater. There is no essential difference in the results obtained, if the initial temperature is varied.

It follows that these solution-droplets, if accompanied by a rising quantity of air, cannot reach the size of raindrops, the masses of which are one or several million times larger than the droplets corresponding to the last whole n calculated here.

Moreover, the concentration of chlorine in raindrops is the same as in the droplets in fogs and clouds, which are millions of times smaller. From this it follows that raindrops never arise from condensation of the droplets in fogs and clouds; if this were the case the concentration of chlorine must of course be enormously small, on the assumption that chlorine salts are nuclei. Even the droplets in fogs and clouds cannot be obtained through direct condensation, since the concentration of chlorine is independent of the size of the droplets. *The increase must take place so that the concentration remains constant.*

From the circumstance that droplets, formed on different α^3 at different vapour tensions and sizes, pass the maximal vapour tension, it follows that at first larger nuclei come into action and then smaller and smaller. A selection of nuclei takes place. In consequence of this and of the results found in the table, the concentration of chlorine must decrease with the height above sea-level. This has been confirmed by the analyses of Lauscher and Lipp. We conclude finally that the number of droplets in fogs and clouds is much smaller than the number of nuclei obtained in Aitkens' Nucleus Counter. This also points to the fact that increase in dimensions of droplets of any particular size must take place otherwise than through direct condensation. Their size must be independent of the concentration. This increase in number perhaps causes that distribution of groups, of which we have spoken above.

THE NATURE OF THE DISPERSOIDS IN COUNTRY AND TOWN AIR.

By J. H. COSTE.

If the atmosphere consisted only of the mixture of gases known as air, conditions on this planet would be very different from what they now are. The characteristics of the air as we know it are largely determined by the very small proportion of solids and liquids which form vast, or merely large disperse systems, in it.

Of these disperse systems some are natural and of meteorelogical significance, whilst others which may or may not be of similar significance are the result of human activities, which they, in turn, may greatly affect. The former class are mainly systems in which water is the major constituent of the disperse phase, whilst the latter are more varied in character. The great dilution of most of these systems, together with the low density and viscosity of the medium, makes investigation difficult, and the systems themselves unstable. The most obvious visual means of investigation have given us classification of clouds, based on Luke Howard's nomenclature, an international scale of visibility and various more or less satisfactory methods of gauging smoke density for the purpose of administering very difficult Acts of Parliament.

Ions and Nuclei.

The study of the conduction of electricity through gases has shown that charges are carried by (a) "small ions" which behave as if they were aggregates of up to 30 molecules (of something) carrying one electronic charge, and by (b) "large" or Langevin ions, similarly charged, but consisting of about a million molecules. The radius of small ions varies from about 3 to 10×10^{-8} cm. and of the Langevin ions from 10^{-6} to 10^{-5} cm., but there is no sharp division, it appears probable that large ions are Aitken nuclei (c) which have captured small ions and thereby become charged. Aitken nuclei, whether charged or uncharged, have a mean radius something under 5×10^{-6} cm.

J. J. Nolan and P. J. Nolan [1] have described a new method of counting small ions which, they claim, yields results with ease and accuracy. Large ions can be determined by differential counts with Aitken's counter, with and without a condenser to remove charged nuclei (ions). Scrase [2] has recently investigated the Aitken counter, in which the number of hygroscopic nuclei is determined by counting the drops falling on a graticule after the adiabatic expansion of a determined volume of air saturated with water vapour. Aitken [3] at first (1879) believed that the hygroscopic nuclei thus counted were dust particles, and continued to call them so after he had realised that they were droplets of unknown

[1] J. J. Nolan and P. J. Nolan, *Proc. Roy. Irish Acad.,* 1935, **42A,** 15-19.
[2] F. J. Scrase, *Quart. J. Roy. Met. Soc.,* **61,** 367-79.
[3] J. Aitken, *Coll. Sci. Papers,* 1923, 34-74.

composition. On this point, M. G. Bennett [4] says " As to the source of the nuclei, there are two obvious possibilities—the sea and chimneys. No doubt the sea provides most of the nuclei operative in genuine sea fogs, and chimneys are able to provide all the nuclei required for town fogs ; but the main source of such nuclei in country air is still a matter under discussion. . . ." N. Fuchs [5] also refers to the lack of knowledge of the nature of large ions :—" *Die einzigen bisher untersuchten amikroscopischen Aerosole waren die sogenannten Langevinschen Ionen, d.h. geladene Teilchen von ganz unbestimmter Natur.*" There is undoubtedly much evidence supporting the view that many of the nuclei found in air everywhere are the result of the evaporation of droplets of sea water projected into it by breaking waves and whirled over the earth by the action of winds. I have repeatedly found chlorions in water condensed from London air and, although these may in part have resulted from the volatilisation of the chlorine often found in some form (not, apparently, invariably, as chlorides) in coal, the sea seems a more prolific source. Rain water, each drop of which had its origin in a nucleus, seems invariably to contain chlorions, [6] as does river water, even in upland and mountainous districts. The water of rivers fed by tropical rains, [7] which usually fall in larger drops than in temperate climates, contains a less concentration of chlorions than that of European rivers, [8] where small raindrops may be considered as more concentrated solutions. The chlorion content of the Thames [8] (before it is contaminated with sewage, which raises the chlorion concentration) is of the order to be expected from the composition of the rainfall and subsequent evaporation. Further, Köhler [9] has analysed the saline content of both clouds and rime (derivatives of nuclei) in the Arctic circle, and based a theory of condensation on the contents of chlorides.

An argument for this theory can be based on the better agreement of the chlorion contents of the rain collected in two deposit gauges a few yards apart at Kew Observatory, as compared with other solid constituents, but this does not necessarily mean that the halogen is derived solely from the sea, since it is probable that the chlorine content of fuel may account for great part of it. In some tentative exeriments I have not so far been able to detect bromine, which constitutes about 0·5 per cent. of the halogen content of sea water, in the Kew deposits.

H. L. Wright and I [10] have investigated the artificial formation of nuclei by burning various fuels (*e.g.* pure alcohol) in an enclosed atmosphere freed from pre-existent nuclei and from sulphur dioxide and other acid gases, and by the electrical heating of metal (*e.g.* platinum) surfaces, and found that formation of nuclei occurred. Of the hypotheses which may be advanced in explanation, the only one which appears to cover all the facts is that droplets of nitrous acid are formed from constituents of the air under suitable conditions of temperature, since this was detected and many nuclei found in the atmosphere after the experiments ; nitrous acid was also found in the condensates. Fuming sulphuric

[4] M. G. Bennett, *Quart. J. Roy. Met. Soc.*, **60**, No. 253, " Some Problems of Meteorology," 114-25.

[5] N. Fuchs, *Acta Physicochimica U.R.S.S.*, **3**, 1935, 61-78.

[6] " The Investigation of Atmospheric Pollution," *D.S.I.R. Annual Reports.*

[7] C. M. Tidy, *J. Chem. Soc.*, **37**, 274.

[8] *Reports of Director of Water Examinations, Met. Water Board.*

[9] H. Köhler, *Gerl. Beit. Geophys.*, 1931, **29**, 168-86.

[10] J. H. Coste and H. L. Wright, *Phil. Mag.*, **7**, 20, 209-34.

acid and sea water were found to be active producers of nuclei when sprayed into air, whilst other liquids were relatively feeble producers of nuclei. G. B. Courtier and I[11] have also found sulphuric acid in the condensate from London air which had been freed from sulphur dioxide. We therefore believe that although sea water is the chief constituent of nuclei in nature, most of the nuclei produced in civilised countries by the fires, furnaces, etc., associated with human activity are droplets of nitrous acid, some sulphuric acid probably being formed also. The formation of sulphuric acid in air containing sulphur dioxide gas with nitrous acid, partly in the gaseous phase and partly in droplets seems inevitable, but a study of sulphuric acid dispersoids in air by N. Fuchs[5] shows that combination occurs easily between droplets, so that a limiting concentration is easily reached beyond which the aerosol becomes unstable, and deposition on surfaces (leading probably to corrosion if they are metallic) occurs. Whether this is the correct, or at least a partial explanation, is difficult to say, but the concentration of sulphuric acid is very small, of the order of 1 per cent. of that of sulphur dioxide, in air.

Further work with Wright* has shown that nuclei in London air may contain the nitric and ammonium ions, as well as those already mentioned. In each case the ions identified were found in condensates from air freed from sulphur dioxide. The known properties of solutions show that any soluble and hygroscopic substance in moist air is likely to yield Aitken nuclei, although at lower tensions of water vapour some solutes will be more effective as drop-formers than others.

The concentration of nuclei in air varies very greatly, but the number per c.c. is generally much less in country air than in that of towns. The concentration over the sea is also usually low. A few figures from various sources will show this, Table I. :—

TABLE I.

Observer.	Place.	Number of Nuclei/c.c.
Aitken.	Top of Rigi.	210 to 3,450.
	Cannes.	1,550 to 150,000.
	Mentone	1,200 to 5,000.
	Lucerne.	616 to 23,000.
	Kingairloch.	205 to 3,100.
	Ben Nevis	335 to 473.
	Garelochhead.	16 to 7,600.
Rankin (quoted by Aitken).	Ben Nevis.	7 (not unusual).
Aitken.	London (garden).	48,000.
	,, (Victoria Street).	150,000.
	Paris (streets).	92,000 to 260,000.
Thellier.		3,500 to 260,000 (average 62,500).
Coste and Wright. 1935-36.	London (County Hall).	23,000 to 200,000.

Wright[12] (Fig. 1) has found a small seasonal variation in the number of nuclei in the air at Kew, the minimum occurring in the summer

[11] J. H. Coste and G. B. Courtier, Paper No. 23.
* *Unpublished.*
[12] H. L. Wright, *Quart. J. Roy. Met. Soc.*, 1935, 61, 71-80 ; and *Geophys. No. 57.*

months June to August.   He also found a distinct decrease as the day advanced from nine hours to fifteen hours.   Mm. Thellier in Paris [13] also found nuclei " *beaucoup moins nombreuses l'apres-midi que le matin*," but observed no marked seasonal variation.

Aitken [14] pointed out that what he called " purifying areas " existed " where most clouds are formed and most rain falls."   In four of these areas he found in the years 1889 to 1893 the lowest number of " particles " in the air coming from

Mediterranean.	Alps.	Highlands (of Scotland).	Atlantic.
891	381	141	72

the averages for these localities being

1611	892	552	338

Over the narrow English Channel (presumably between Calais and Dover) he found 7000, but Bennett states that "the numbers of large ions and Aitken nuclei at sea (about 200 per c.c.) are very much less than over land."

The mean mass of a nucleus is less than 1×10^{-15} gm.   J. J. Nolan and V. H. Guerrini [15] have recently found that the radius of the nuclei in Dublin air is $2 \cdot 85 \times 10^{-6}$ cm. and their mass $1 \cdot 68 \times 10^{-16}$ gm.   The mass of the nuclear content of the air, even when the number is up to 10^{6}/c.c., is of the order of 10^{-5} of the water content of saturated air.

FIG. 1.—Seasonal variation of dust particles and nuclei at Kew, 1928-30 (Wright).

Fog and Cloud are derivatives of nuclei, formed by condensation on them of water vapour.   M. G. Bennett [4] gives the limits of radius of fog droplets as from 4×10^{-4} cm. to 3×10^{-3} cm., with velocity of falling from 0·2 to 11 cm./sec. and of cloud drops an upper limit of 1×10^{-2} with a velocity of falling of 121 cm./sec. remarking " it is seen that a small fog droplet falls so slowly that it may be regarded as almost permanently suspended, and even in the case of a large drop, a current

[13] O. Thellier, *Comp. Rend.*, **201**, 348-50.
[14] J. Aitken, *Coll. Sci. Papers*, 397-9.
[15] J. J. Nolan and V. Guerrini, *Proc. Roy. Irish. Acad.*, 1935, **43A**, 2·5-24.

of air rising with quite a reasonable velocity would be sufficient to maintain it at a constant height."

When air contains, besides natural dispersoids, tarry or sooty particles, coalescence occurs to a greater or less extent and, since fog is usually associated with still air conditions, the concentration of smoky particles becomes very high and the fog assumes the yellow to black hue well known to dwellers in large towns. Since most fuel contains sulphur, the concentration of sulphur dioxide and to a less extent of sulphuric acid becomes high, and the fog is irritant as well as dark. The variation of sulphur dioxide and black suspensoids during the fog of 23rd December, 1935, in London, is shown for part of the day in Fig. 2. With a temperature inversion over and around a large city the combined
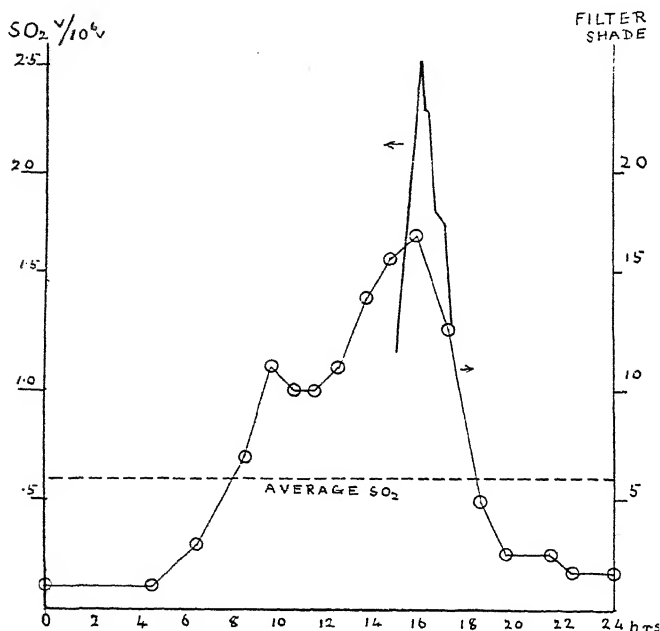
FIG. 2.—Owen's filter shade and SO_2 at County Hall, London, during foggy day, 23rd December, 1935.

result of this and the heating effect of many warmed buildings may cause an overhead fog with darkness but reasonable clarity in horizontal directions. Professor Firket will speak on the effect of such a sulphurous fog in the Meuse valley.

Rain Drops as the ultimate derivatives of nuclei, may reach a radius of about 0·27 cm. (approximately the maximum calculated from the surface tension of water against air), and fall through air with a terminal velocity of about 800 cm./sec. Even such a large drop must spend a considerable number of seconds in falling from a cloud to the surface of the earth, and smaller drops spend much longer. During its fall, a drop is likely to become associated with other dispersoids in the air, and Dr. F. J. W. Whipple and I have found * that rain water collected

* *Unpublished.*

in a clean vessel contains appreciable amounts of salts and of insoluble matters. Some portion of the salts is accounted for by the hygroscopic nuclei on which drops form, but insoluble matters can only be derived from suspensoids in the air. The fact that considerable amounts of soluble and insoluble solids are found in water collected in deposit gauges used for investigation of atmospheric impurity [6] can hardly be adduced as proof that rain itself actually contains other non-aqueous matter than is derived from nuclei, since some may have been washed from dust falling into the gauges in dry periods, but all the matter collected in these gauges is derived from dispersoids in the air, and it may amount during a month to kilogrammes per square dekametre.

The nature of this solid matter (some of which is undoubtedly proper to the nuclei) is investigated, in a limited way, under the scheme of the Atmospheric Pollution Committee, the deposits of soluble and insoluble matter being determined and separated into tar, carbonaceous matter other than tar, sulphates, chlorides and ammonia. I have found on microscopical examination of the insoluble matter collected in London deposit gauges : spheres of fused matter—some glassy with gaseous inclusions, some opaque and light coloured with a warty surface, as if bubbles of gas had reached the periphery and burst as the mass solidified, some of magnetic iron oxide, others of coke, sintered sausage-shaped particles also evidently formed at a high temperature, coal, charred wood, textile fibres, plant hairs and other vegetable tissues, sand mostly from quartz, less often from flint, and occasionally scales of lepidoptera.

The Finer Solid Dispersoids of Air can be determined with reasonable accuracy by dust counters of which the Owens jet instrument [6] and the thermal precipitation instrument designed by Whytlaw Gray and Green [6] are the most efficient, or by Owens' air filter,[6] which is applicable only for black (soot) particles, in which the stain on paper through which a known volume (usually 2 litres) of air has been filtered, is compared with the stain produced by a known mass of carbon. An interesting investigation was carried out by H. G. I. Robins in the country around Norwich, and the results were discussed by Professor David Brunt,[16] who found (*inter alia*) that " the pollution is greatest in winter, least in summer, and intermediate (and equal) in spring and autumn," and " reaches an approximately steady value, showing no further diminution, at a distance estimated at 4 miles in spring, 5 miles in summer and autumn and 6 to 7 miles in winter." Brunt also concluded " that the cloud is effectively 4 or 5 miles wide at 3 miles from the city. As it is at least 2 miles wide initially, this result is not surprising."

The quantity of dispersed matter collected on the cover glass of a dust counter or the paper of an air filter is too small for ordinary microchemical analysis, but I have *qualitatively* examined stains filtered on ashless paper from several cubic feet of air in the manner suggested by G. M. B. Dobson.

Calcium carbonate and sulphate were found, in addition to soot and tar, in stains obtained by Dobson at Oxford, and kindly placed at my disposal ; no free acid was found by him when the stains were fresh, but the presence of calcium carbonate and sulphate accounts for this, as calcium carbonate is likely to be present in air in amount enough to neutralise any acid droplets which come in contact with it, and which are most probably present, though, as Courtier and I show in another paper, only in very small amount.

[16] D. Brunt, *The Invest. Atmo. Poll*, *17th Report*, 50-58.

Living Matters.

An interesting and important group of suspensoids found in air comprises living and dead organisms and organic structures. Bacteria, moulds (spores), spores of ferns, pollen grains and infusoria in the loricated state may fairly be considered as dispersoids, but it would hardly be legitimate to include seeds with pappi or winged animals.

Bacteria and moulds in air have been investigated by many workers, but the subject has received no systematic attention. My colleague, Dr. J. Graham Forbes, F.R.C.P., examined the bacterial and hyphomycete content of the air of the London tube railways,[17] and with the exception of one or two pathogenic species of aspergillus among the moulds, no definitely pathogenic organisms were identified out of the large number of colonies examined. W. F. Wells has studied air borne infection.[18].

Interesting proof of the distribution of fern spores in air can be seen in the growth of ferns in the neighbourhood of the electric light bulbs lighting the Cheddar caves and Kent's Cavern at Torquay. I found an interesting case of air-borne vegetable suspensoids at Arcachon. The streets were strewn, in places where dust could collect, with a bright yellow, sulphur-like powder; it was also on the sands of the seashore. Examined microscopically, it was indistinguishable from the pollen of *pinus maritima*, grown in the forests along the Basque coast for the production of turpentine. The appearance of growths of *protococcus viridis* and, rarely, of the red variety *hæmococcus* in any stagnant water, whether in a waterbottle or a roadside puddle, and on the bark of trees is evidence of its widespread occurrence in air, and of the readiness with which it will settle out under quiet conditions.

Hygroscopic nuclei and the finer dispersoids, sooty or otherwise, are found in greater quantity in town than in country air. This is only to be expected, since the higher numbers are always associated with fire, which is a relatively rare phenomenon in nature. An exception should, perhaps, be made of volcanic districts, but I have found no observations on this point, except the ascription of various phenomena to the dust projected into the air in the Krakatoa eruption. The few specimens of Krakatoa dust which I have seen were very coarse, and could not have remained in the air for long.

The relatively large vegetable suspensoids may mostly be derived from country sources, but few observations of atmospheric impurity have, it seems, been made on country air, compared with the large number on town air. I hope in the near future to be able to work on country air. It may, however, be remarked that the leaves of plants in towns are usually covered with dust (largely of the kind associated with chimneys), whilst leaves in the country (now that our roads are no longer dusty), are seldom obviously dusty.

Characteristic Town Suspensoids, above the dimensions of nuclei and soot or dust-counter particles (from, say, 1 to 1000 μ) mostly result from combustion of solid fuel, and consist of silicates (if from industrial furnaces usually spheres, showing complete fusion of the fuel ash, or sintered particles) with particles having the characteristic foam structure of coke and sometimes covered with minute spheres of ash.* Ash from

[17] J. Graham Forbes, *J. Hyg.*, 1924, 22.
[18] W. F. Wells, *et al*, *Amer. J. Hyg.*, 1934, **20**, 611-18 ; *ibid.*, 619-27.
* If combustion had gone on further, they would either have coalesced or become free spheres ; domestic fires, on the other hand, where the temperature is lower, yield a flaky or shaly ash.

pulverised fuel furnaces, usually consists of spheres which are often hollow, or at least contain gas inclusions, although long sintered particles are sometimes seen. This hollow form causes them to have a lower apparent density than would be expected of silicates,[20] but grinding in an agate mortar will bring up the density and show " postage stamp fractures " where bubbles of gas have been broken. It is rather remarkable that pulverised fuel ash often contains a very appreciable proportion of unburnt coke. Another characteristic constituent of ash from high temperature furnaces is magnetic oxide of iron in spheres or sintered fragments ; they contain ferrous and ferric iron, and are readily magnetised. That this has been fused indicates a temperature of about 1600° C.

Some notion of the nature of the coarser dispersoids falling through the air can be gathered from examination of the insoluble matter collected in the standard deposit gauges. Those in the London parks collect spheres, indicating industrial pollution, with coke and amorphous or laminar " ash," probably from domestic grates, some coal and charred wood from the same source, textile fibres, with vegetable hairs and tissues of horticultural origin. The Kew deposits are more definitely horticultural and domestic, with small spheres, few in number, due to industry. All contain quartz sand. Leaves from a marsh around a power station burning pulverised fuel showed lodgements of spheres along the midrib, some of magnetic oxide, whilst leaves from Teddington Railway Station were covered with ferric oxide with some spheres ; the ferric oxide I attribute to the erosion and corrosion of the live rails of the electrified system ; few steam trains pass through this station. Dust collected from leaves and from a raised wooden platform in my garden at Teddington, contained much sand, and some coal and coke, with very few spheres. Dust from leaves in Battersea Park, near the Power Station, was mostly domestic and horticultural in origin, very few spheres being found, showing the efficiency of the gas washing plant. Ivy leaves from sheltered places around the village of Cockington, near Torquay, yielded a fine, reddish sand, with calcium carbonate, chlorides and traces of sulphates, vegetable hairs and tissues, unicellular green algæ and mycelia, but no obvious ash, coke, coal or soot.

The chemical and microscopical analyses (Table II.) of grit (a) from the roof of a London railway terminus, taken during a cleaning ; (b) from the

TABLE II.

	(a)	(b)	(c)
Water			4·81
Tar (soluble in CS₂)	1·07	2·20	
Oxidised oils (? soluble in acetone)	0·81 ⎱	29·40 ⎱	
Other carbonaceous matters	28·45 ⎰		32·79 ⎰ (spanning b/c)
Ferric oxide	12·31 ⎱		4·75
Alumina	12·25 ⎰	11·05	4·40
Calcium oxide		9·11	8·65
Alkalis, etc.	3·68 ⎱		
Soluble silica	1·78 ⎰	14·84 ⎱	17·97
Insoluble silicious matter	39·65	33·40	26·63
	100·00	100·00	
Including SO₃		9·01	9·11

inner part of the Fleche at County Hall, London ; and (c) from the air washing plant of the Council Chamber, will show the nature of the disperse phases which reach a considerable height in the air of London.

Microscopical Examination.

(a) Coal, coke, sand, spheres (glassy and bubbly, some yellow, mostly white or transparent) ferromagnetic particles.

(b) Wood, vegetable branched hairs and other tissues, sand (rounded and sharp, ferric oxide (magnetic) with very little Fe_3O_4, very few spheres and very little coal or coke.

(c) Mostly amorphous coal ash, very few spheres, coke, trace of coal, felted textile fibres, plant hairs and tissues, charred wood.

The composition of dust in the underground railways of Paris is given in a report by Armand Gautier, Laveran, Vallin and Bès de Berc to *le Conseil d'Hygiène publique et de Salubrite du Department de la Seine*.[19] It is interesting to note, as in the London dust from the station roof that the tunnels of the " Metro." contained large proportions of iron, whilst in the Nord-Sud organic matter predominated.   See Table III.

TABLE III.

"Metro."		
Fer metallique.	46·00	soit fer total 56·15 per cent.
Oxide de fer.	14·57	
Cuivre.	traces.	
CaO (en SO_4 Ca).	12·12	
Matiere grasiere.	1·12	
Eau et matieres organiques.	12·60	par difference.
"Nord-Sud."		
Cuivre.	neant.	
Fer metallique.	traces.	
Fer oxyde.	8·06	
Soit en fer total.	5·64	
Silice, etc.	19·80	
Sulfate de chaux, $CaCl_2$, etc. (en SO_4Ca)	26·80	
Eau et matieres organiques.	45·30	

The calcium chloride is ascribed to the salt used for washing the platforms, and the organic matter to the material of the brakes.

Lessing [20] has given much information on the dust emitted from industrial chimneys in a paper read before the World Power Conference in 19 , and the emission of soot, ash, grit and gritty particles and the measures taken to obviate such emission is the subject of a report, published in 1932, of a Committee appointed by the Electricity Commissioners.[21]

[19] A. Gautier, *Comp. Rend. Cons. d'Hyg. Pub. et du Salub. du Dept. de la Seine*, 1914, **20**, 197–242.
[20] R. Lessing, *Fuel in Science and Practice*, Aug., 1930, **9**, 348.
[21] *Elec. Comm. Report on . . . Soot, Ash, Grit and Gritty Particles. . . .* H.M.S.O., 1932.

Summary.

The dispersoids found in the air are partly normal to it. These have water for their main constituent. Others which are natural in origin, but are associated with air which has travelled over land, are living cells. The air of towns, or which has travelled over towns, contains droplets formed from the gaseous products of combustion, and tar, soot and ash from the combustion of fuel. Fine silicious matter may be found in the air of town or country. The concentrations of these dispersoids, even in highly polluted air, are very low.

GENERAL DISCUSSION. *

Mr. C. F. Goodeve (*London*) : asked what was meant by the " unstable size " referred to. The discussion of the equilibrium conditions obtaining in droplets, given both by Köhler and by Dooley and the speaker in papers to this discussion, indicates the existence of no such unstable size with the properties described by Dobson.

Professor F. G. Donnan (*London*) said he thought that modern workers would do well to study the classical work of Willard Gibbs on the thermodynamics of " surfaces of discontinuity." It was extraordinary how little people knew about the profound investigations of Gibbs on the formation and stability of films and liquid drops.

Professor H. Köhler (*Uppsala*), in introducing his paper, added: (1) The latent heat of condensation, λ, mentioned on page 1157, is derived as follows :—

The energy equation requires

$$q = dU + Apdv \qquad . \qquad . \qquad . \qquad . \quad (1)$$

where U is the internal energy of the system and $Apdv$ the work in heat-units performed by the system. We now bring in T and x as independent variables:

$$dU = \frac{\partial U}{\partial x} d + \frac{\partial U}{\partial T} dT \qquad \text{and} \qquad dv = \frac{\partial v}{\partial x} dx + \frac{\partial v}{\partial T} dT.$$

Dividing (1) by T, we obtain the change of entropy dE.

$$dE = \frac{q}{T} = \left(\frac{\partial U}{\partial T} + Ap \frac{\partial v}{\partial T} \right) \frac{dT}{T} + \left(\frac{\partial U}{\partial x} + Ap \frac{\partial v}{\partial x} \right) \frac{dx}{T}. \qquad . \quad (2)$$

Since dE is a whole differential. we get :—

In (3) the latent heat of condensation is :—

If, now, we insert the tension and the specific volume of the drops and the vapour, we get :—

$$\lambda = \lambda_0 + \frac{2AT^2v'}{r} \frac{\partial}{\partial T}\left(\frac{s}{T}\right) - AR_1T \times \frac{\partial \log e}{\partial x}.$$

The latent heat of condensation on droplets of a solution, λ, is derived without assuming any change of the entropy, but from the energy equation and from the fact that dE is a whole differential.

(2) The number, N, of droplets mentioned in my paper is the same as the number of nuclei accompanying the rising air, and the system is cooled

* On the three preceding papers.

adiabatically. On this assumption, the process is reversible. One must remember that change of entropy is entirely determined by the initial and terminal values. I have not examined isothermal processes.

(3) According to theory, a relation should exist between the concentration and the number N. This I have never found experimentally. I therefore conclude that the growth of droplets must take place otherwise ; if coalescence take place (or evaporation from some droplets and simultaneous condensation on others) the process is irreversible.

Mr. C. F. Goodeve (*London*) : Asked why Köhler applied thermodynamical equilibrium considerations to his droplets but denied that equilibrium obtained during the condensation of the fog to form hoar frost. *Microscopic* investigations could not *prove* that the hoar frost had the same composition as the fog from which it was deposited, and experiments in other cases have shown that equilibrium conditions are very rapidly set up. The speaker considered it essential to prove this point before consideration could be given to the extensive data obtained by Köhler.

The whole-number rules were very interesting, and further experiments showed intermediate series. How was it possible to reconcile this whole-number rule with the thermodynamical considerations given later in the paper ?

The conclusion with regard to the latent heat of evaporation in the unstable region (where the slope was negative), Fig. 1, is of doubtful validity. Droplets in this region are very unstable, as is pointed out in a later paper by Dooley and Goodeve. It is not useful to apply entropy considerations to a system which is essentially irreversible.

Mr. J. H. Coste (*Teddington*) said : The chlorion content of rainwater has been determined in many places. I think Professor Köhler would find much information in Clarke's *Data of Geochemistry*. The water of large rivers in tropical districts, and of upland streams, is of the order given by Professor Köhler for rainwater, which would be expected. I find, on looking at the analyses published by the Atmospheric Pollution Research Committee that there is a tendency for the chlorion content of rainwater in towns to be higher in winter than in summer. How far this is due to salt brought in by wind from the sea, or alternatively to chlorine from coal is difficult to say, but the halide content of fuel is by no means negligible.

Professor F. G. Donnan (*London*) said that some eminent landscape painters had drawn his attention to the haze which always existed in England with an East wind. He could confirm these observations from his own experience. His artist friends found it impossible to paint when the East wind (fine weather) haze blotted out all detail. As soon as the wind changed to the South or West, this particular haze disappeared. Was it due to Continental or other dust nuclei which remained in suspension in the relatively dry air-currents of the East wind, and which were rapidly deposited by adsorption or absorption of water from the moist, southerly and westerly air-currents ?

This peculiar and very intense haze was quite different from ordinary mists or fogs, or from the well-known " sea frets " which sometimes invaded the land areas.

Dr. F. T. Peirce (*Manchester*) said : Would the landscape painter distinguish between light scattering by particles and refraction by convection currents, which may be more pronounced in East wind weather when the upper air is cold and the ground warmed by bright sunshine ?

Dr. R. Meldau (*Berlin*) said : Almost a hundred years ago, Chr. G. Ehrenberg described " the abundant invisible air-borne organic life " which he had studied, described and pictured over a period of many decades.[1] Svante Arrhenius developed along similar lines the hypothesis of the

[1] *Abhand. Königl. Akad. Wiss., Berlin*, 1871 *et seq.*

Panspermie (*Allbesamung*). It might perhaps be useful to review the old work of Ehrenberg in the light of modern knowledge.

Dr. W. H. J. Vernon (*Teddington*) (*communicated*) : An indication of the nature of dispersoids in country and town air is afforded by the wind-borne constituents of certain metallic corrosion products, *e.g.* the familiar green patina on copper.[2]

ANALYSIS OF WIND-BORNE MATERIALS IN THE GREEN PATINA ON COPPER FROM TYPICAL SOURCES.

	N. Mimms Spire, Hertfordshire.	Bodleian Library Roof, Oxford.	British Museum Dome, London.	Customs House Dome, Ramsgate.
Per cent. wind-borne matter in green patina . . .	9·6	6·9	19·2	4·3
Per Cent. Constituents in Wind-borne Matter.				
Iron oxides (as Fe₂O₃) . .	43·0	64·3	24·2	36·6
Alumina, Al₂O₃ . . .	47·4	13·4	37·0	17·0
Carbonaceous matter . .	6·4	11·9	32·6	9·7
Siliceous matter . . .	3·2	10·4	6·2	36·6

The high proportion of iron oxide and alumina is striking, although it is difficult to deduce any topographical relationship ; well-marked maxima are exhibited by carbonaceous matter in the town sample, and by siliceous matter in the marine sample.

The nature of the dispersoids has also a great influence in determining the composition of the main part of the product, *i.e.* the part derived from corrosion of the underlying metal. The characteristic constituent in country atmospheres (in Great Britain) is basic copper sulphate, derived mainly, no doubt, from the action of sulphur dioxide either in gaseous or dispersoid form, although ammonium sulphate particles must play a subsidiary part.[3] In town atmospheres the proportion of basic copper carbonate is very greatly increased, rising to nearly 25 per cent., compared with 2·7 per cent. in rural atmospheres, due in part at least, to a higher proportion of carboxylic acids in town air,[4] almost certainly in dispersoid form ; but, as suggested by Mr. Coste,[5] this factor is probably supplemented by the greater amount of calcium carbonate diffused into town air, from mortar, cement, limestone, etc.

Although particles of chlorides derived from the sea provide effective nuclei for rain drops at much greater distances, they cease to be effective from the corrosion point of view at comparatively short distances from the sea, unless they are favoured by prevailing winds. Thus, at inland sites in this country chlorides are absent from the copper patina. In samples taken in mid-Wales, 30 miles from the sea, there is 20·75 per cent., and at Dundalk, on the north-east coast of Ireland, only 8·1 per cent. basic copper chloride. The occurrence of the greater chloride at the greater distance from the sea is here clearly attributable to the influence of prevailing winds.

It seems right to emphasise the undoubted importance of dispersoids in atmospheric corrosion phenomena, especially as this aspect has not been formally represented elsewhere in the discussion. The fundamental part

[2] Vernon and Whitby, *J. Inst. Metals*, 1930, **44**, 389.
[3] G. F. New, J. S. Owens, W. H. J. Vernon, *ibid.*, 1932, **48**, 130, 137, 140.
[4] W. H. J. Vernon, *J. Chem. Soc.*, 1934, 1853.
[5] J. H. Coste, *J. Soc. Chem. Ind.* (*Chem. and Ind.*), 1934, **53**, 1061.

played in the corrosion of iron by suspended particles (sufficiently small to have Brownian movement and capable of interception by a simple muslin screen) was demonstrated by the writer some years ago,[6] and its importance has been amply confirmed in more recent experiments.[7]

Professor H. Köhler (*Uppsala*), in reply, said : Without doubt there are different kinds of hygroscopic nuclei in the atmosphere. According to my calculations, the larger nuclei of a definite kind must first be considered, and then smaller and smaller : the mass is decisive. If different kinds of nuclei are present, however, the mass is not of paramount importance, but their respective hygroscopic powers also come into consideration. In large towns and undustrial countries the atmosphere gains many very hygroscopic nuclei, are emitted into the atmosphere, and these have the same effect as the less hygroscopic seasalt.

My results on condensation and the constitution of clouds, appear to conflict with thermodynamics, which has not been uncommon in meteorology since Hertz 1884. If we assume that condensation on adiabatic expansion of the air takes place on nuclei which are present, results are obtained which do not correspond with reality. Droplets cannot grow by continuous condensation to the size of raindrops, or even to that of cloud droplets.

The latent heat of condensation is deduced for condensation on droplets consisting of pure water.[8]

The vapour tension of the droplets of solutions for the condition $\alpha^3 < \alpha_1{}^3 . 2^{-13}$ decreases or to some extent is almost constant on adiabatic cooling, it is also a function of T. Smaller seasalt-nuclei than $\alpha_1{}^3 . 2^{-13}$ are not available for the condensation in the atmosphere, because too great supersaturation then would be necessary. It is also important when considering equilibrium conditions to define accurately the vapour tension of a droplet present in the atmosphere, with regard to the measured mean value of the pressure of the water vapour.

The constitution of the hoar-frost deposited from fog, has been examined in other than microscopic ways and the same results were always obtained.[9]

Mr. J. H. Coste (*Teddington*), in reply, said : Sir Robert Robertson had informed him in correspondence of the work on products of combustion to which he referred at the meeting. It was interesting to receive this confirmation of the frequent presence of nitrous acid in air contaminated with smoke from chimneys. Dr. Vernon's figures seemed to show that wind-borne matters, and especially silicates and carbon were more prevalent in town air.

As to the products of corrosion of copper he was inclined to think that the basic copper sulphate was a residual product, since he had found crystals of normal copper sulphate, on copper surfaces exposed to the air and dew, but not to the leaching effect of rain.

He was very interested in what Dr. Meldau had to say about Ehrenberg, whose microscopical work was well known, with whose researches on atmospheric dispersoids he was not acquainted. The early microscopist, Leowenhoek, had made some evidently very careful examination of the dispersoids in rainwater, and Angus Smith had done a great deal. He would seek the opportunity of reading Ehrenberg's papers.

[6] W. H. J. Vernon, *Trans. Faraday Soc.*, 1927, **23,** 159.

[7] *Ibid.,* 1935, **31,** 1678.

[8] W. Voigt, *Thermodynamik*, II Band, p. 134.

[9] See my papers from 1921 to 1933 and also the examination of rain made by Israel and Niederdorfer.

THE DETERMINATION OF THE MASS AND SIZE OF ATMOSPHERIC CONDENSATION NUCLEI.

BY J. J. NOLAN AND V. H. GUERRINI.

In 1903 J. J. Thomson [1] and Langevin [2] independently demonstrated the possibility of the existence in a non-saturated atmosphere of stable drops of water of diameter of the order 10^{-6} cm. In 1905 the large atmospheric ions were discovered by Langevin and were found to be of a certain degree of homogeneity as regards their mobility. It was natural, then, to assume that the large ions were the condensation nuclei, familiar owing to the work of Aitken, which had acquired positive and negative charges, and that the condensation nuclei were the stable uniformly-sized drops, the theoretical possibility of which had been indicated. Whatever be the nature of the condensation nuclei, the identification of the large ions with the charged nuclei may be said to have been firmly established by all later work.

In 1917, J. J. Nolan showed [3] that, assuming the large ions to be spheres of water, calculations of their size made by a kinetic-theory formula due to J. J. Thomson and by Millikan's modification of the Stokes-Cunningham formula were in good agreement. For ions of mobility 0·00033 cm./sec. in a field of 1 volt/cm., assumed to carry unit electronic charge, the radius calculated was $4·1 \times 10^{-6}$ cm. The fact that the charge on the large atmospheric ion is normally the electronic charge was afterwards demonstrated.[4] More recently, J. J. Thomson and G. P. Thomson,[5] from calculations somewhat similar to those already referred to, obtained the value $4·5 \times 10^{-6}$ cm. An interesting calculation of a different kind might be mentioned. By attributing the absorption of solar radiation to the condensation nuclei, P. J. MacLaughlin [6] from experiments made at the top and bottom of the Eiffel Tower, calculated a value $5·5 \times 10^{-6}$ cm. for the radius of the nuclei.

The possibility of making more precise measurements of the nuclei was disclosed as a result of some observations [7] directed in the first instance towards the investigation of the manner in which nuclei are lost from an air-stream flowing through tubing. It appeared that the loss of nuclei could in general be attributed to two effects, gravity and diffusion to the walls. It was possible also in general to separate these effects, to estimate the amount of each separately, and hence to deduce the terminal velocity of fall of the nuclei and their diffusion coefficient in air.

[1] J. J. Thomson, *Conduction of Electricity in Gases,* 1st ed., 1903, p. 149.

[2] P. Langevin, *Cours de Collège de France,* 1903-04, *vide* A. B. Chauveau, *Le Radium,* 1912, **9,** 161.

[3] J. J. Nolan, *Proc. Roy. Soc.,* 1917, **97A,** 112.

[4] J. J. Nolan, R. K. Boylan and G. P. de Sachy, *Proc. Roy. Irish Acad.,* 1925, **37,** 1.

[5] J. J. Thomson and G. P. Thomson, *Conduction of Electricity in Gases,* 3rd ed., 1928, p. 189.

[6] P. J. MacLaughlin, *Comptes rendus,* 1927, **184,** 1183.

[7] J. J. Nolan and V. H. Guerrini, *Proc. Roy. Irish Acad.,* 1935, **43,** 5.

Experimental Methods.

In order that the losses of nuclei should be sufficient to enable accurate observations to be made, it is necessary that the air carrying the nuclei should pass very slowly through a rather narrow channel. The most convenient way to secure this is to cause the air to flow in a thin sheet between parallel plates. By building up a pile of plates with suitable separators, several such air-sheets may be arranged to flow in parallel. When the planes of the plates are horizontal, the loss of nuclei is due both to diffusion and fall. When the plates are set with their planes vertical, the loss by fall is negligible and diffusion alone may be held to operate.

In our experiments a water-sealed gasometer of capacity about 500 litres was filled with a mixture of filtered air and atmospheric air containing the nuclei under examination. The air in the gasometer, having a concentration of about 5000 nuclei per cm.³, was driven, under a suitable head of pressure through the parallel-plate system. At the inlet and outlet of the system, the number of nuclei per cm.³ of air was counted by an Aitken apparatus. Each determination of velocity of fall and of diffusion coefficient involved a large number of readings of the Aitken instrument at each end of the apparatus under the two conditions of plates horizontal and plates vertical.

Calculation of V_g, the Velocity of Fall.

If we assume a uniform concentration of nuclei in the air entering the apparatus and conditions of stream-line flow in the space between the plates, it is easily shown that the fraction k of nuclei lost is connected with the terminal velocity V_g by the relation

$$V_g = \frac{6Q}{Lb}\left(\frac{k^2}{2} - \frac{k^3}{3}\right)$$

where Q is the volume of air passing per second between the plates, L is the horizontal length and b the breadth of the space.

Since the quantity k (fraction of nuclei lost by fall) is obtained as the difference between the fractions lost in the horizontal and vertical positions of the plates, it is in general small, and is not readily determined to a high degree of accuracy. The amount of agreement between the experimental and the theoretical loss by fall obtainable under favourable conditions may be judged from Fig. 1, in which values of k obtained with various values of the air-stream are plotted. The continuous curve shows the theoretical relation between the quantities for an assumed velocity of fall of 8×10^{-5} cm./sec.

10   20
Q.   cm.³/sec.
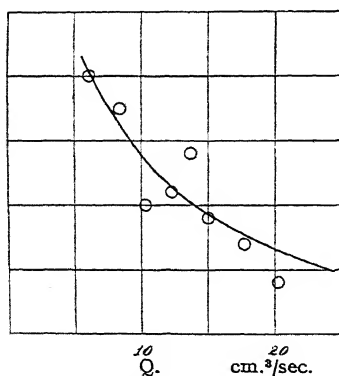
FIG. 1.

Calculation of D, the Coefficient of Diffusion.

It has been shown [7] that the loss of particles by diffusion from air flowing through a thin rectangular channel may be expressed in the form

$$\overline{aQ} \qquad 0\cdot0065 \exp. \qquad \overline{aQ}$$

where n/n_o is the ratio of the concentrations of the particles in the air entering and leaving, b is the breadth, z the length and a the half-depth of the channel and Q is the volume of air passing through per second. Since the second term will, in practice, always be negligibly small, the relation can be expressed as

$$n/n_o = 1 \cdot 066 \exp. - x, \quad \text{where} \quad x = 3 \cdot 67 \, bDz/aQ.$$

From the nature of the observations, it is to be expected that the determinations of D, the diffusion coefficient will be of a higher order of accuracy than those of V_g. The values found do, in fact, exhibit a higher degree of consistency. Fig. 2 shows values of n/n_o, obtained
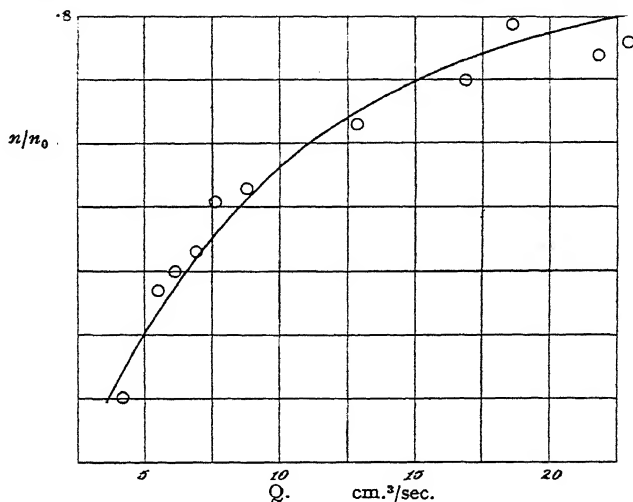
FIG. 2.

under conditions not specially favourable, plotted against Q, the volume of air passing per second. The continuous line shows the theoretical relation between the quantities for an assumed value $D = 18 \times 10^{-6}$ cm.^{2}/sec.

It appears generally from our observations that the loss of nuclei can be completely accounted for by the two processes of fall and diffusion, and that the processes can be separately observed. In our experiments three sets of apparatus differing widely in dimensions were used. The particulars of the materials and dimensions of these are set out in the following table :—

Apparatus.	Material of Plates.	Thickness of Plates.	Length.	Breadth.	Depth.	Number of Channels.
I	Glass .	0·211 cm.	76 cm.	19·0 cm.	0·211 cm.	7
II	Duralumin	0·046 ,,	100 ,,	24·9 ,,	0·642 ,,	7
III	Brass .	0·054 ,,	30 ,,	9·9 ,,	0·054 ,,	10

The results of observations made on nuclei in Dublin air are collected in the following table. It should be stated that the air was not drawn

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directly from the open. It was room air, not contaminated in any way, but differing from atmospheric air in that the nuclei in it were older on the average than those in the outside air.

The values set out in this table are means derived from figures which, especially in the case of V_g, show very considerable scatter. This variation in the values found may be regarded as due in part to

Apparatus.	$V_g \times 10^5$ cm./sec.	$D \times 10^6$ cm.^{2}/sec.
I. 1st Series	8·6	17·5
2nd ,,	6·9	18·1
II.	8·2	20·9
III.	7·2	17·4

the inherent experimental difficulties, and in part to the fact that the observations were spread over many months, with very varied weather conditions, and possibly considerable real variation in the character of the nuclei. It is satisfactory that the mean values found with the different apparatus are in fair agreement. We may conclude with a certain measure of assurance that the values V_g and D for the nuclei we have been observing are close to

$$V_g = 7 \cdot 5 \times 10^{-5} \text{ cm./sec.}$$
and
$$D = 18 \times 10^{-6} \text{ cm.}^2/\text{sec.}$$

Calculation of Mass and Size.

The well-known Einstein equation gives the mobility, *i.e.* the ratio of the velocity of a particle through a gas to the force acting on it $= DN/RT$ we have therefore

$$\frac{V_g}{mg} = \frac{DN}{RT} \quad \text{and} \quad m = \frac{V_g}{D} \cdot \frac{RT}{ng}.$$

The mass of the nuclei observed in our experiments is therefore

$$m = \frac{7 \cdot 5 \times 10^{-5}}{18 \times 10^{-6}} \cdot \frac{831 \times 10^5 \times 288}{6 \cdot 06 \times 10^{23} \times 980}$$
$$= 1 \cdot 68 \times 10^{-16} \text{ g.}$$

If we assume that the nuclei are spherical we can write the Einstein equation in the form

$$D = \frac{RT}{N} \quad \frac{+ l/a \, (A + B \exp. - ca/l)}{6\pi\eta a}.$$

Knowing the constants in this equation, we can use it to calculate a for different values of D. Values of A, B and c have been given by Millikan[8] and Mattauch[9] While these values differ, they give, over the range with which we are concerned, curves of D against a which are practically identical. From these curves we find for $D = 18 \times 10^{-6}$, $a = 2 \cdot 85 \times 10^{-6}$ cm. The volume of such a particle will be $0 \cdot 97 \times 10^{-16}$ cm.^{3}. Comparing this with the value $1 \cdot 68 \times 10^{-16}$ gr. found for the mass, we arrive at $1 \cdot 68/0 \cdot 97 = 1 \cdot 7$ for the density of the nuclei.

Effect of Time.

The values for mass and radius which we have just given are calculated from the results of a great many experiments, all made on room air, and refer therefore to nuclei to some extent aged. During the

[8] R. A. Millikan, *Physic. Rev.*, 1923, **22**, 1.
[9] J. Mattauch, *Z. Physik.*, 1925, **32**, 439.

duration (about two hours) of each experiment, the nuclei were contained in a water-sealed gasometer. There was no indication that, during the time of the experiment, any change in the nuclei occurred. On long standing however the evidences for change are quite definite. There is a reduction in the values of both V_g and D. If V_g and D fell off at the same rate, *i.e.* so as to keep V_g/D constant, it would mean that the nuclei were increasing in size, but that their mass was remaining constant. Our observations made so far tend to show that V_g diminishes more rapidly than D, so that it would appear that the nuclei surviving after a certain lapse of time are (1) larger, (2) of smaller mass, and therefore (3) of considerably lower density than the average at the beginning. It may be noted that P. J. Nolan [10] found that nuclei stored in the same way showed an increase with time in their coefficient of combination with small ions. These results are consistent with the supposition that the nuclei present originally are a mixture of different kinds, and that those observed after a lapse of time are the larger and lighter ones which have escaped loss by diffusion and fall.

Observations on Nuclei in Country Air.

We have made a number of observations on nuclei in the air at Glencree in the Wicklow Mountains, eleven miles south of Dublin. Here the concentration of nuclei varies over a wide range, large numbers being found when the air-supply comes from the direction of Dublin, while small numbers are usually found when the wind comes from the open country to the south and west. The results found so far indicate the possibility of a considerable range of variation in the sizes and masses of the nuclei. Observations are being continued with the object of determining the effect of the size of the nuclei on the control which they influence on the equilibrium of atmospheric small ions.

[10] P. J. Nolan, *Proc. Roy. Irish Acad.*, 1929, **38**, 49.

GENERAL DISCUSSION.

Professor F. G. Donnan (*London*) said he thought that the work of Professor Nolan and Dr. Guerrini represented a very important contribution to the problem of the nature of atmospheric condensation nuclei.

Dr. G. M. B. Dobson (*Oxford*) said : The minute particles seen in the normal atmosphere by the aid of the ultra-microscope appear to be of various sizes. Indeed, it would be very surprising if they were all closely the same size, as assumed by Professor Nolan in his calculations. In his observations with the plates of the instrument horizontal the particles which settle out will be chiefly the larger ones, while with the plates vertical the smaller particles will diffuse to the sides most rapidly. Thus, if the particles present have a large range of size his equations will not hold strictly.

I should like to suggest to Professor Nolan that he should make calculations to see what would be the effect on the results obtained if there were really present particles of many sizes. Thus, it would be interesting to know how the size he would obtain by the present method would differ from the true average size of the particles present.

Professor R. Whytlaw-Gray (*Leeds*) said : The distinction usually made between atmospheric nuclei and finely dispersed solid matter appears to me to be an artificial one. It is supposed that the former, on account of their hygroscopic character, condense moisture readily and form minute droplets, whilst the latter do not behave in this way at all, or do so only

with difficulty. For this reason the Aitken counter is supposed to in-numerate the hygroscopic nuclei only, and the Owens' dust counter and the thermal precipitator the larger particles of solid material which are of microscopic dimensions.

Experiments made here with the Aitken instrument indicate that solid particles of such materials as silica, magnesium oxide, finely divided carbon, etc., readily act as condensation nuclei and can be counted and it seems probable that this method reveals not the hygroscopic nuclei only but the total number of particles of all kinds that are present.

Again, the view is often expressed that nuclei are of amicroscopic dimensions and hence are invisible in the ultramicroscope. Some of them no doubt fall into this category, but many nuclei and large ions can be seen and counted with the latter instrument. Support for these views is afforded by a comparison recently made in this laboratory of the Aitken counter with the ultramicroscope on a number of smokes and dusts. With smokes of stearic acid, carbon black, and paraffin, as well as with silica dusts, a close agreement was found. With ordinary Leeds air containing the usual amount of suspended pollution, the Aitken instrument counted about 30 per cent. more particles but when the air was enclosed in a large tank and comparisons made at intervals over a long period, the numbers counted became closer with lapse of time and at the end of three hours were approximately equal by the two methods.

These experiments appear to show that particles of various kinds and of a considerable size range are present in town air. Of these a certain proportion are amicroscopic and a much smaller proportion of microscopic dimensions. The most numerous are those which are usually classed as ultramicroscopic and fall approximately between the size limits of 5×10^6 and 2×10^{-5} cms. radius, $i.e.$, between 0·05 and 0·2 μ.

The total number of particles observed in Leeds air when these experiments were made, was of the order of 10^5 per c.c. Those visible microscopically in the thermal precipitator records numbered about 3000 per c.c.

Professor F. A. Paneth (*London*) said : On the question whether particles of different size are to be found in air, I should like to know the opinion of meteorologists concerning the presence of particles too small to be seen even under the ultra-microscope. So far as I am aware, such particles have been postulated only by chemists, as a means of explaining variations in the density of air found in 1893 by Lord Rayleigh and more recently (1917) confirmed by Ph. A. Guye in Geneva ; according to Guye, the weight of 1 litre of air can vary by several tenths of a milligram. If due to a difference in composition, this would correspond to a change in the oxygen percentage of more than 0·1 per cent. by volume which, of course, could readily be detected chemically ; it is impossible to ascribe the density variations to any other alteration of the chemical composition of air. They seem to be connected with changes in the barometric pressure, and Guye suggests that the assumption of extremely fine particles of dust may provide an explanation. This, of course, is an *ad hoc* hypothesis made only after the failure of all other attempted explanations, and I wonder whether any meteorological observation can be quoted in its support.

Professor R. Whytlaw-Gray (*Leeds*) said, in reply : It is difficult to imagine any kind of fine particulate system present in air which would alter the density by as much as a few tenths of a milligram per litre, $i.e.$, by a few parts in 10,000 ; the variation reported by Guye in the experiments quoted. In a fine smoke containing about 10^6 particles per c.c. an average value for the mass concentration is of the order of 20 milligrams per cubic metre. This could only alter the density by 1 part in 70,000, though its presence would be evident in the Tyndall beam. If the air were optically empty the particles would have to be about ten times smaller and even this small variation in weight would require a number concentration of 10^9 per c.c. which seems very unlikely.

Mr. G. W. Slack (*Leeds*) said : A variation of only one-tenth of a milligram corresponds to a mass concentration of one hundred milligrams per cubic metre and whilst a cloud of this concentration could no doubt be prepared which would give no sign of its presence in the Tyndall beam or ultramicroscope there can be little doubt that it would aggregate sufficiently to do this in a very short time, and so it is unlikely that this is the explanation of the observed variations.

Mr. A. G. Grant (*Darlington*) said : Has any attempt been made to define the properties of a nucleus ? Previous papers have referred to hygroscopic nuclei, for example, sea-salt, and it has often been suggested that organic spores and particles of free carbon (in industrial fogs) may form nuclei. Professor Nolan's paper deals with molecular aggregates which are presumably somewhat bigger than Langevin ions. Are these aggregates credited with condensation properties resembling the hygroscopicity of sea-salt, or is there some more basic attribute which determines whether or not the smallest aggregates of matter may serve as nuclei ?

Mr. J. H. Coste (*Teddington*) said : There seems no reason, in the nature of things, why hygroscopic nuclei should, in the air of inhabited districts, be all of the same kind or size. Wright and I have found various ions (in the chemical sense) in the condensates from London air, with some evidence of selective condensation. Professor Nolan has said that the density of $1\cdot7$ of the nuclei is not a figure on which much reliance can be placed, although it is of the right order. It would correspond to very strong solutions of any likely salt or hydride, and seems to be too high.

Mr. C. H. Bosanquet (*Billingham*) said : Are the diffusion and fall effects additive ? It appears probable that the increase of particles striking the lower plate would be almost compensated by the decrease on the upper plate, if the velocity of fall is small. If this is the case, erroneous values of V_g would be obtained by applying the formula for k given in the paper directly to the values of k obtained by difference.

Dr. J. J. Nolan (*Dublin*), in reply, said : We have not been concerned in this work very directly with the nature of the condensation nuclei, but rather with an essay at the determination of the sizes of the bodies—whatever they may be—which are counted by the Aitken instrument. We have hitherto accepted the sharp distinction, apparently established by the work of Wigand and Boylan, between the condensation nuclei and the true dust. The question, however, is obviously an open one, and we await Professor Whytlaw-Gray's further results with great interest.

In the course of correspondence, it has been pointed out to us by Mr. Bosanquet that in the calculation [7] of V_g while we have allowed for the difference in air-velocity in different levels of the air-stream, we have not taken account of the same difference as affecting the velocity of entry of particles into the apparatus. This consideration gives a simpler expression for V_g, and as a result of the correction (while a greater degree of coherence appears among the values calculated for different air-velocities), the results for velocities of fall are approximately doubled.

From experiments now in progress on atmospheric air contained in oil-sealed gas-holders, we hope to obtain a truer idea of the distribution of sizes of nuclei in the free atmosphere.

HYGROSCOPIC NUCLEI IN THE FORMATION OF FOG.

BY JAMES C. PHILIP.

The fogs which have been the subject of investigation by the author and his collaborators [1] are those obtained on passing an air stream charged with a volatile acid through a solution of alkali hydroxide containing a trace of volatile alkali. When, for example, filtered air is drawn through concentrated hydrochloric acid and then through a solution of sodium hydroxide to which a trace of ammonium chloride has been added, a fog is produced in the alkali vessel, and this fog, once formed, is extraordinarily persistent. It can be passed through water without more than partial absorption and although passage through strong sulphuric acid appears to clear up the air stream, the fog reappears on subsequent bubbling through water.

The fog droplets can be removed from the air stream by woolly asbestos and submitted to analytical examination. This shows them to contain ammonium chloride and free hydrochloric acid and the weight of fog, obtained in a standard run, has been found to vary in a significant manner with the concentration of the alkali solution and with the amount of ammonia which it contains. The formation of fog can be detected even when the proportion of ammonia in the alkali solution is as low as 1 part in 10 million. Indeed, the production or non-production of fog under the conditions stated, provides as delicate a test for the presence of ammonia as the well-known Nessler reagent.

Our view of this phenomenon is that as the bubble of the air-HCl stream forms on the end of the inlet tube in the alkali solution molecules of ammonia from the latter combine with molecules of hydrogen chloride in the bubble producing nuclei of ammonium chloride; water then condenses on these hygroscopic nuclei, and the droplets so formed absorb free hydrogen chloride. On the bubble rising to the surface the suspended droplets escape into the vapour space above the solution, thus giving rise to the fog.

The point with which this communication is more particularly concerned is the question of the mechanism of formation of the droplets. Light is thrown on this matter by studying the manner in which the weight of fog and its composition are affected, under otherwise steady conditions, by changes in the vapour pressure of the alkali solution. As this vapour pressure is reduced it will be increasingly difficult for the nuclei to acquire water, and the weight of the fog droplets obtained in a standard run will decrease. Such a result has been obtained with sodium hydroxide solutions of greater strength than $1\cdot0N$ concentration, but the most interesting evidence was provided by a series of experiments in which the vapour pressure of the alkali solution was reduced by the addition of sodium chloride.

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[1] Askew, *J. Chem. Soc.*, 1927, 966 ; Aldis and Philip, *ibid.*, 1930, 1103 ; Jackson and Philip, *ibid.*, 1934, 341.

The data recorded in Table I. were obtained in a series of experiments [2] all carried out with $N/1$ NaOH solution containing 0·001 per cent. NH_3, but differing in the content of sodium chloride. It should be noted that each figure in the second column includes 80–90 mg., due to the water vapour.

The figures in the foregoing Table clearly indicate that as the fog obtained in a standard run gets thinner the amount of acid which it contains falls off steadily, whereas there is no sign of decrease—there is in fact a slight increase —in the amount of

TABLE I.

NaCl, g.-equiv./1.	Weight of Fog + Water Vapour mg.	Found in Fog.	
		HCl (free), mg.	NH₃ (as NH₄Cl), mg.
0	467	35·9	0·64
1·0	457	37·0	0·64
2·0	389	33·4	0·65
3·0	310	28·4	0·65
4·0	217	18·9	0·66
5·0	140	12·0	0·66

ammonia carried over as ammonium chloride. It seems reasonable to conclude that the hydrogen chloride carried over depends on the water content of the fog droplets and that if the water-vapour pressure of the liquid in the fog-chamber could be reduced much further, nuclei of ammonium chloride would still be produced which, however, would be both dry and neutral.

Observations confirmatory of those in Table I. were obtained with triethylamine as the volatile alkali instead of ammonia.[3] In the series detailed in Table II. the air-HCl stream was passed in each case through a solution which was 0·5N as regards sodium hydroxide and contained 0·0009 per cent. triethylamine. The solutions, however, were progressively richer in sodium chloride.

Here again, as the water-vapour pressure of the solution in the fog-chamber decreases the free acid carried over in the standard run falls steadily, whereas the quantity of amine tends to rise.

TABLE II.

NaCl gm. – equiv./lit.	Wt. of Fog + Water Vapour (in mg.).	In Fog.	
		HCl Free mg.	Amine mg.
0	524	36·7	0·65
1·0	459	34·7	—
2·0	385	30·7	0·66
3·0	297	24·4	—
4·0	182	14·8	0·67

A relevant qualitative observation may also be recorded. A dried air-HCl stream was passed through a 50 per cent. NaOH solution containing 0·001 per cent. NH_3 then through two sulphuric acid bubblers and then through water. Nothing was visible above the sodium hydroxide solution, but fog appeared in the water vessel. It contained no detectable free acid.

The foregoing evidence certainly supports the view that the primary event in the production of the fogs is the formation of nuclei of ammonium chloride followed by the condensation of water on these nuclei, giving a solution of salt. Only then does the absorption of hydrogen chloride begin. It is true that ammonium chloride is usually regarded as non-deliquescent, but the description is not an absolute one, for the possibility of deliquescence depends not only on the nature of the salt

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[2] Jackson and Philip, *loc. cit.*[1]   [3] Banfield, *unpublished experiments.*

but also on the vapour pressure of its saturated solution and on the relative humidity of the surrounding atmosphere. Further, when the salt is in an extremely finely divided state, as in the present case, and has therefore a relatively large surface exposed, the rate of adjustment of equilibrium between the salt and the water vapour in the surrounding atmosphere will be very high. The experiments of Owens [4] on the conditions of deliquescence of minute crystals exposed to air of different relative humidity have shown that in the case of such salts as sodium chloride and ammonium chloride there is, in fact, a rapid adjustment of equilibrium.

[4] *Proc. Roy. Soc.*, 1926, 110A, 738.

GENERAL DISCUSSION.

Mr. C. F. Goodeve (*London*) said : Professor Philip and his co-workers have been studying a very interesting type of mist and have developed a satisfactory explanation, involving the formation of a nucleus of ammonium chloride. It is to be hoped that they will now put their theories to a quantitative test. Some of the ways in which this can be done have been indicated in a paper by Dooley and myself.

It seems likely that the hydrochloric acid mist formed under the conditions of their experiments was in equilibrium with the vapour over the solutions which they used. Neglecting the effect of curvature, the vapour pressure of a solution of hydrochloric acid, as indicated by the 2nd and 3rd columns in Table I. should be the same as that of the NaCl-NaOH solution given in column 1. I have calculated the vapour pressures of these solutions (by adding the vapour pressure lowering of each compound) and in general have found that there is not good agreement between the values so calculated. It seems that there may be some disturbing factor present in their experiments.

No explanation has been given of the constancy of the ammonia content in the mists (last column, Table I.). It seems that this may be due to either or both of two causes. If the reaction between HCl and ammonium in the gaseous phase is very fast, the concentration of ammonia will be negligibly small. The amount appearing in the mist will therefore be governed by the rate of evaporation of ammonia from a solution of a certain strength into a gaseous space free from ammonia. This rate will probably be independent of the sodium chloride concentration and, therefore, a constant value is to be expected. On the other hand, the amount of ammonia in the mist is 80 per cent. of the total originally present in the liquid, and, as the rate of evaporation is probably directly proportional to the concentration of ammonia, a smoothing out of any variation would result from its deficiency.

The condensation of water and hydrogen chloride on the ammonium chloride nuclei must occur simultaneously as the vapour pressure of water on the droplet must always be below that of the solution before it is able to take up more water.

Mr. J. H. Coste (*Teddington*) said: The concentration of HCl in the fog water seems to have been fairly constant around 8 per cent., with a tendency to be greater in the fogs containing less ammonium chloride, suggesting that the droplets when formed absorbed a proportion of HCl, mainly determined by the concentration of gas, but also by the concentration of chlorions already existing in the droplets. Wright and I found that hydrochloric acid alone evaporated into nucleus-free air did not produce nuclei, which could be counted in the Aitken counter, although Helmholtz found that it did produce the " blue " cloud when mingled with steam issuing from a jet.

Professor J. C. Philip (*London*) said, in reference to Mr Goodeve's suggestion of some disturbing factor in the experiments : The results of these experiments, carried out under specified and controlled conditions, were perfectly definite and regular, and the want of agreement between the calculated vapour pressures was probably due to the uncertainty of the assumptions underlying the calculations.

He agreed with Mr. Goodeve's view that the amount of ammonia in the mist would be governed by the rate of evaporation of ammonia from the alkaline solution. It was probable, however, that the escaping tendency of the ammonia would, if anything, increase with the sodium chloride concentration, and this would account for the slight rise in the figures of the last columns in Tables I. and II.

As to the contention that the condensation of water and hydrogen chloride on the nuclei must occur simultaneously, the experiments indicated that a dry ammonium chloride mist (haze) would carry no free hydrogen chloride and hence it seemed fair to conclude that the absorption of water (it might be to some minimum extent) must precede the absorption of any hydrogen chloride. Subsequent to this the absorption of water and hydrogen chloride would no doubt go on simultaneously.

In reference to Dr. Coste's experiments with hydrochloric acid, it was perhaps of interest to record that in his (Professor Philip's) laboratory also it had been confirmed that strong hydrochloric acid did not fume in moist air, freed carefully from dust and ammonia.

SORPTION OF FOGS BY LIQUIDS.

By H. Remy (*from experiments with* W. Seemann, A. Panceram *and* H. Friedland).

Received in German (18*th March*, 1936), *and translated by* James Colvin.

The factors which influence the sorption of suspended matter on passage through liquids, filters or, even, empty vessels are, firstly, *sedimentation*, and, secondly, the collisions of the suspended particles with the walls or with the surrounding medium ; the latter may be conditioned either by the individual movement of the particles (Brownian motion) or by the *turbulence* of the gas transporting them.

For suspended matter (such as the sulphuric acid fogs we have investigated), Brownian motion may be excluded at once as a decisive factor since, with particles of the diameter shown by this fog (10^{-4} cm.), it is far too slight relative to the observed decrease in concentration.[1] On the other hand various observations have been made which suggest that in such fogs sedimentation plays an essential part in the decrease in concentration on passing through the sorption apparatus ; for example, damp fogs are less absorbed by solutions, the higher the concentration of the solution, and consequently the lower its vapour pressure ; [2] again, the decrease in concentration of the fog in passing through a wash-bottle depends almost linearly on the reciprocal of the streaming velocity, *i.e.*

[1] *Cp*. H. Engelhard, *Z. Elektrochemie*, 1925, **31**, 590.
[2] H. Remy and K. Ruhland, *Z. anorg. Chemie*, 1924, **139**, 51 ; *cp*. also A. Winkel and G. Jander, *Schwebestoffe in Gasen*, p. 72 f. (Stuttgart, 1934).

on the time taken to traverse the wash-bottle.[3] The experiments communicated here show, however, that this interpretation is not valid. Under experimental conditions such as we employ, sedimentation plays, at most, a quite subordinate part in the decrease in concentration of the fog. On the other hand, our experimental results are in complete agreement with the assumption that the essential factor is the turbulence of the transporting gas.

The experiments show that the dependence of the fall in concentration of the fog on the height of the layer of liquid through which it is bubbled is given accurately by assuming that the contact of the particles with the liquid depends solely on turbulence, and that sedimentation plays no part. The different sorptive action of solutions and pure water is therefore not to be attributed to an effect on the sedimentation velocity (as a consequence of reduction in the size of the particles by loss of water). Moreover, the dependence of the sorption on the streaming velocity in our experiments must be ascribed not to the influence which the time taken to pass through the sorption apparatus has on the amount of sedimentation, but to the dependence of the bubble size on the streaming velocity.

I. The Dependence of the Decrease in Concentration of the Fog on the Height of the Layer of Liquid through which it is Bubbled.

If a gas bubble carrying a fog rises with uniform velocity through a liquid, the number of particles coming into contact with the enclosing liquid as a consequence of turbulence within the bubble in the time interval dt (the time required to travel the distance ds) is proportional to the number of particles in unit volume. The concentration decrease in the fog is thus given by the equation :

$$- dc = a \cdot c \cdot ds,$$

where c is the concentration and a is a proportionality factor. Assuming uniform turbulence (by maintaining constant experimental conditions), the concentration decrease produced by traversing the interval s is

$$- \int_{c_1}^{c_2} \frac{dc}{c} = \int_0^s \quad := - \ln \frac{c_2}{c_1} = a \cdot .$$

$$(1b) \quad c_1 - c_2 = c_1(1 - e^{-a \cdot s}).$$

The difference between the concentration, c_0, of the fog on entering the sorption vessel and the concentration, c_e, on leaving was measured. This measured decrease in concentration consists of (1) the decrease $c_0 - c_1$, which the fog undergoes from the moment of entry to the moment at which it begins to rise with the gas bubble through the fluid, (2) the decrease $c_1 - c_2$, whilst it ascends through the liquid, and (3) the decrease $c_2 - c_e$, which ensues as the upper part of the sorption apparatus, where there is no liquid, is traversed.

$$c_0 - c_e = (c_0 - c_1) + (c_1 - c_2) + (c_2 - c_e) \quad . \qquad . \qquad . \quad (2)$$

If the experimental conditions, apart from the height of the column of fluid are kept constant, then

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[3] H. Remy and C. Behre, *Kolloid Z.*, 1935, **71**, 129 ; H. Remy and W. Seeman, *Kolloid Z.*, 1935, **72**, 3.

where b_1 and b_2 are constants dependent on the experimental conditions. Substituting these in equation (2), and combining with equations (1a) and (1b), we obtain :

$$\text{,} - c_e = c_0 . \qquad - b_1)(1 - \qquad \cdot c_0(1 -$$

$$- \ln\Big(1 \qquad\qquad \frac{}{- b_1)(1 - b_2)}\Big).$$

Transforming from natural to common logarithms, and expressing the concentration decrease as a percentage of the initial concentration, we obtain

where $'$. 100.

Of the two coefficients, α is a measure of the absorption occurring during passage through the fluid, whilst β permits the calculation of the fall in concentration of the fog before and after this process.

Fig. 1 shows how accurately the linear dependence of the expression

$$- \log \frac{100 - A}{- - -} \quad \text{on the}$$

of the column of demanded by equation (3) is verified in our experiments using fogs of sulphuric acid, with water as the sorbent liquid. If sedimentation played a decisive part during the ascent of the bubble through the liquid, a curve should have been obtained, since in such

FIG. 1.—Dependence of the absorption of the fog on the height of the column of liquid through which it is bubbled.

clouds a substantial initial increase in the sedimentation velocity can be observed.[4]

A preliminary condition for good reproducibility of measurement is that the cloud should be produced under the same atmospheric pressure as that at which it enters the liquid, and that fluctuations of pressure during an experiment are carefully to be avoided.

Equation (3) permits the determination of the concentration decrease which the fog undergoes *whilst bubbling through the liquid*, from a few xperiments carried out with different heights of liquid. It makes

[4] H. Remy, *Z. anorg. Chemie,* 1924, **138,** 167.

possible the elimination of the other concentration changes consequent on passing through the sorption apparatus. Theoretically, experiments with two different heights of liquid suffice, although in practice a larger number are employed in order to exclude chance errors.

In equation (3) α has the dimensions of reciprocal length. By multiplying $\frac{1}{\alpha}$ by log 2, we obtain the height of liquid column required to reduce the fog concentration in the bubble to one half. In the experiments included in Fig. 1, this height was 24·0 cm. ($\alpha = 0·0125, \beta = 0·017$).

Similarly by varying the height of the space which the fog has to traverse after passing through the liquid to the outlet of the sorption apparatus, that part of the concentration decrease occurring there may be determined. In the experiments of Fig. 1 this height was 5 cm. For a liquid column (water) of 10 cm. (measured from the orifice of the inlet tube), A was found to be 27·90 per cent., of which 3·24 per cent. was due to the concentration decrease in the fog prior to its ascent through the liquid, 24·20 per cent. to the decrease during passage through the liquid and only 0·46 per cent. to the decrease in the part of the sorption apparatus not filled with liquid. With a liquid column of 25 cm. under the fixed conditions, the concentration decrease above the liquid amounted to only 0·32 per cent. of the initial concentration in a total decrease of $A = 50·29$ per cent. The concentration decrease which the fog experienced between the times of leaving the liquid and escaping from the sorption apparatus was thus relatively slight, whereas that which occurs up to the moment at which single bubbles begin to rise through the liquid, is by no means negligible.

FIG 2—Dependence of the absorption coefficients α and β on the concentration of the solutions used for absorption of the fog.

II. Sorption of Sulphuric Acid Fogs by Sulphuric Acid and by Caustic Potash Solution.

Our experiments have shown that equation (3) holds for both sulphuric acid and caustic potash solutions as absorption fluid, the co-

efficients α and β being affected in approximately the same way by the nature of the absorption fluid. This is shown by Fig. 2. Clearly, therefore, for the coefficient β, the decisive factor is the decrease in concentration of the fog which takes place, during the *time of formation of the individual bubbles* by absorption on the liquid boundaries.

Under the experimental conditions of Fig. 2, using pure water as absorption liquid, the coefficients had the values $\alpha = 0.0077$ and $\beta = 0.089$. Using 6.1 per cent. sulphuric acid, α fell to 0.0046 and β to 0.050. Using 5 per cent. caustic potash solution, $\alpha = 0.0025$ and $\beta = 0.016$. With further increase in concentration of the absorptive fluid, the rate of diminution of absorptive power fell off, as Fig. 2 shows. In Table I. are summarised the heights of the columns of liquid, by passing through which under the experimental conditions of Fig. 2 a fall in concentration of 50 per cent. is occasioned. (Half-value heights.) Thus 51 per cent. sulphuric acid possesses a five times smaller absorptive power, and 40 per cent. caustic potash solution, a $6\frac{1}{2}$ times smaller absorptive power than pure water.

TABLE I.—HALF-VALUE HEIGHTS OF DIFFERENT ABSORPTION FLUIDS.

Absorption Liquid.	Water.	Sulphuric Acid.			Caustic Potash.		
		6.1 Per Cent.	11.9 Per Cent.	51.25 Per Cent.	5 Per Cent.	10 Per Cent.	40 Per Cent.
Half-value height in cm.	39.1	66.1	89.4	202	119	196	257

The concentrations of the solutions in Table I. were so chosen that the sulphuric acid solutions and the caustic potash solutions had the same specific gravity. This was done in order to test whether solutions of the same specific gravity possess equal absorption coefficients ; they do not, and there is just as little agreement in absorptive powers of solutions of sulphuric acid and caustic potash when compared at equal viscosity, equal surface tension or at equal vapour pressure.

III. Dependence of the Fog Aborption Coefficients on the Streaming Velocity of the Fog.

The results communicated in the two preceding sections were obtained using a streaming velocity of 0.2 litres per minute. The absorption fluids were contained in vertical glass tubes of 3.6 cm. width and of different lengths.

A second series of experiments was carried out at *different streaming velocities*, using Drechsel flasks as absorption vessels. Table II. clearly shows that α is dependent on the streaming velocity. It increases almost linearly with the reciprocal of the streaming velocity, *i.e.* with the reciprocal of the streaming velocity the bubble size decreasing [5] correspondingly. The dependence of α on the streaming velocity is thus brought about by the fact that the size of the gas bubble in which the fog rises through the absorption liquid, is dependent on the streaming velocity. This cannot be ascribed to the fact that the amount of sedimentation of the fog is affected by changing the streaming velocity, since

[5] H. Remy and W. Seemann, *Kolloid Z.*, 1935, **72**, 283.

in contrast to α, the coefficient β exhibits *no* such dependence on the streaming velocity, as would necessarily become apparent, if the concentration decrease were dependent to any real extent on sedimentation, since the time taken for the fog to pass through the sorption apparatus was varied ten-fold.

TABLE II.—THE ABSORPTION COEFFICIENTS α AND β AT DIFFERENT STREAMING VELOCITIES OF THE FOG.

Streaming Velocity in Litres Per Min.	0·1.	0·133.	0·2.	0·4.	1·0.
α	0·0301	0·0249	0·0192	0·0113	0·0076
β	0·04	0·05	0·02	0·04	0·04

The preceding statements support the view that the β-values are determined essentially by the concentration decrease of the fog before it bubbles through the liquid. The possibility of sedimentation after passage through the liquid was excluded in the experiments summarised in Table II., by keeping the empty space in the wash-bottle as small as possible (13 c.c.). If this small volume is exceeded to any considerable extent, sedimentation in this space may occur at low streaming velocities and affect the value of the sorption found under these conditions.

GENERAL DISCUSSION.

Mr. C. F. Goodeve (*London*) (*communicated*) : Remy's attempt to distinguish between sedimentation on one hand, and Brownian motion and turbulence on the other, does not seem to have a very good basis. One usually considers that Brownian motion is quite distinct from the other two factors. If one increases the particle size and mass, the removal by sedimentation *and* by turbulence increases very rapidly, whereas the removal by Brownian motion decreases. If this fact is agreed, the conclusions that appear in the second and third paragraphs are not valid.

It does not seem to be very useful to choose the complicated conditions which arise in bubbling a fog through a liquid. This is borne out by the fact that Professor Remy's mathematical equations show that there is no agreement between the absorbing power and any one of the physical or chemical properties of the absorbing liquid. It would be much better to choose simpler conditions such as occur when one passes a fog *over* a liquid surface at known velocities under reproducible conditions. Experiments in an apparatus of this type are described in a later paper to this discussion by Dooley and the speaker.

Dr. N. Fuchs (*Moscow*) (*communicated*) : I regret very much that I could not become enlightened personally as to the sense in which Remy uses the word " turbulence." It could hardly be used in the strict hydrodynamical sense, since within air-bubbles of some millimetres size the turbulent state could only be attained at such flow-velocities of the air as are practically impossible in the case considered. It seems therefore that Remy means by " turbulence " the irregular motion of the air within the bubbles which leads to continual intermixing, and to uniform distribution of the mist contained in them. If this is so, the exponential law of absorption of mists by liquid layers of different height found by Remy must hold good independently of the actual mechanism of the adsorption.

The intermixing of the mist cannot, however, by itself force the droplets to reach the walls of the bubble. For this the droplets must leave the

flow-lines of the air directed tangentially to the walls, which is possible under the action of three factors only (assuming the droplets are uncharged), *viz.*, Brownian movement, gravity and centrifugal force. It seems that Remy has in view the latter. It is, however, easy to see that the effect due to centrifugal forces is small in comparison with sedimentation in the case considered here.

Near the walls of the bubble the droplets move under the action of centrifugal force with velocity $w = mvB/r$ where m and B are the mass and the mobility of the droplets, v velocity of air-flow in the bubbles, r their radius. The velocity of fall of the droplets is equal to mgB.

Assuming $r = 0.4$ cm. (the average size of air-bubbles in Remy's experiments) we come to the conclusion that both effects will be equal at $v = 20$ cm./sec. It is hardly possible to admit the existence of such flow-velocities within air-bubbles of such dimensions.

It seems, therefore, that sedimentation must play the chief rôle in the absorption of relatively coarse aerosols by liquids. It is, however, clear that sedimentation accompanied by continuous intermixing of the mist, now under consideration, is substantially different from sedimentation in still air, although the rate of settling at a given concentration of the mist should be practically equal in both cases. The only difference is that in the second case the rate of settling is constant (assuming the iso-dispersity of the mist and the absence of coagulation), and in the first it changes exponentially with time.

This conclusion could be verified quantitatively if the exact size of the droplets in the experiments of Remy were given. Assuming 1μ to be for the radius of droplets and 8 mm. for the diameter of the bubbles we can calculate that in 5 sec. about 20 per cent. of the mist will be absorbed owing to sedimentation.

Remy says later that if the absorption were caused by sedimentation of the mist then, according to his earlier experiments, there would be an acceleration of absorption during the rising of the bubbles. This statement seems to me not quite correct, since the time during which the bubbles move through the liquid in Remy's experiments [1] is so short (8 sec.) that there cannot be any perceptible coarsening of the mist.

Professor H. Remy (*Hamburg*), in reply, said : Removal by Brownian motion was excluded in my experiments by the particle size. The only possible causes of removal therefore, were sedimentation and turbulence. In the case of sedimentation we must distinguish between what happens during the rise of the bubble through the liquid and what happens in the liquid-free space of the absorption apparatus. The experiments described in the first and second paragraphs, exclude the influence of the latter effect ; those in the third paragraph prove also that sedimentation within the bubbles has had no essential influence on the removal of particles since, with increasing of the streaming velocity, the times of formation of the bubbles decrease from 0.15 to 0.03 sec. The coefficient β in the experiments of the Table II. must therefore decrease considerably, if the removal of particles had been caused only by sedimentation, whereas, if turbulence had been the essential factor, β would be constant, because in this case the decrease caused by the shorter time would be paralysed by the increasing of the turbulence caused by the higher velocity of the air current. The word " turbulence " signifies the irregular motion of the air within the bubbles.

The " complicated " conditions of our experiments were given by the problems before us ; we were not only studying the question discussed in this paper but a number of other questions, the results of which will soon be published in the *Kolloid Zeitschrift*.

It is true as Dr. Fuchs says, that my experiments do not decide what is the nature of the forces moving the particles through the air film in the

[1] Remy, *Kolloid. Z.*, 1935, **72**, 285.

neighbourhood of the bubble wall ; as I have said in my paper, this question is as yet unsettled.

In the experiments of the first paragraph, the volume of bubbles was 0·48 c.cm., the initially falling velocity of the particles on entering the absorption apparatus was $3·5 \times 10^{-3}$ cm./sec. If sedimentation only, without turbulence in the bubbles had taken place, the decrease of concentration in 8 secs. would have been 36 per cent., whilst 99·85 per cent. was found. According to earlier experiments,[3] the falling velocity of the mist particles increases initially proportionally with time. Consequently, the decrease of concentration caused by sedimentation, must follow an equation of the form $- \, dc = (a_1 + a_2 t)c \cdot dt$, instead of $- \, dc = a \cdot c \cdot dt$. These questions will be discussed in the above-mentioned forthcoming papers.

[3] H. Remy, *Z. anorg. Chemie*, 1924, **134**, 167.

FOG ALONG THE MEUSE VALLEY.

By J. Firket, Professor at the University of Liége.

From the 1st to 5th of December, 1930, a thick fog covered a large part of Belgium, along the Meuse (flowing from W.S.W. to E.N.E.), between Liége and Huy, about 15 miles above it. A large number of people were injured ; several hundred were severely attacked with respiratory troubles, and 63 died on the 4th and 5th December, after only a few hours of sickness. Many head of cattle had to be slaughtered. On the 6th of December the fog disappeared ; the respiratory troubles improved and, in general, rapidly ceased. Public opinion was deeply moved, not only in Belgium, but also in neighbouring countries. Wherever fogs of several days duration are frequent, public authorities were anxious to know the causes of this catastrophe and several delegates were sent to the spot. This apprehension was quite justified, when we think that, proportionally, the public services of London, *e.g.*, might be faced with the responsibility of 3200 sudden deaths if such a phenomenon occurred there.

A public enquiry was opened on 6th December and a group of five Liége University professors, Messrs. Dehalu, Schoofs, Mage, Batta and Firket, brought to this question their special knowledge of meteorology, toxicology, industrial chemistry and pathology. These experts had at their disposal the most complete means of investigation because the examining magistrate could require autopsies and have all doors and documents opened to him.

There follows an abstract of the objective statements and interpretations to which the experts came.

Medical Observations.—All the sick people felt a retrosternal pain spreading along the edge of the ribs ; they all had fits of coughing, dyspnœa of a paroxystic and expiratory character such as asthma, or real polypnea, although the latter was less frequent.

Among those in whom asthma was particularly severe, or who previously had frequent asthmatic bronchitis, or even who had cardiac insufficiency or myocarditis, or again who received anti-asthmatic treatments too late, the respiratory troubles were complicated by cardio-vascular collapse, marked by a rapid pulse, pallor, cold extremities, profuse per-

spiration and sometimes, when it had been looked for, dilation of the heart. In the sick, whose respiratory troubles did not consist in attacks of asthma, but in quickening of the rhythm of breathing, cyanosis was observed, as well as a tendency to frothy sputum.

About fifteen autopsies with microscopical examinations of tissues and spectroscopical or spectrographical analyses of blood, and also toxicological analyses of all organs were performed. The histological examinations showed that noxious products had been inhaled in the last hours of life, and had brought on a local and superficial irritation of the mucous membrane of the respiratory ducts exposed to the air inhaled. The microscopical sections of the lungs showed, in addition, the inhalation of fine particles of soot even as far as the pulmonary alveoli.

It is to be noted that the first symptoms, shown by the first patients, began in the afternoon of the third day of fog, which had then been at its maximum opacity for several hours. On the other hand, on the 6th of December, when the fog dispersed, respiratory troubles grew rapidly better, so that death took place only on the fourth and fifth day of the fog. Moreover, the enquiry established that the first symptoms, marked by the first patients treated, were observed at the same time along the whole of the attacked region, *i.e.*, for about 15 miles. It was thus impossible to discern the " diffusion " of a noxious gas in the atmosphere of the valley.

Meteorological Conditions.—The meteorological conditions existing from the 1st to 5th of December were as follows : Fog, starting on December 1st, anticyclonic conditions persisted, characterised by high atmospheric pressures and feeble wind, generally in an easterly direction, *i.e.*, blowing upstream and slowly spreading smoke coming from the city of Liége and the large factories above it into the narrow valley. Moreover, a phenomenon of inversion of temperature established at about 90 yards from the soil a kind of atmospheric ceiling, lower than the hills bordering the valley and thus transformed the valley itself into a tunnel. The total volume of this tunnel could be approximately calculated therefore. Fine solid particles, mainly made of soot, had fallen during the five days of fog into the almost motionless atmosphere. Most of them—varying from 2 to 6 μ—must have taken two or three days to fall from the height of 40 to 70 yards, if we apply Stokes's law ; 60 yards is the average height of the manufactory chimneys or the industrial region in question.

The conjunction of meteorological conditions observed in the beginning of December, 1930, is quite unusual in this district. During the last thirty years, fogs lasting more than three days have only occurred five times, always in winter (1901, 1911, 1917, 1919 and December, 1930). It is interesting to note that, because of the war, industry was not very active in 1917 and 1919, while in January, 1911, serious accidents occurred similar to those of 1930, but with attacks chiefly on cattle.

Chemical Analyses.—Since the fog itself could not be analysed, the chemists sought to ascertain the nature of the gas by analysis of deposits on the soil, but this was unsuccessful since they could not, in this way, distinguish the toxic substances which had been deposited only during the recent foggy period.

They established the balance of the gases which had polluted the atmosphere of the valley, by taking into account the activity of the factories of the region, as well as the number of domestic fires. For the factories, the raw materials used during the five days of fog and in many cases, intermediate products of gas and smoke were examined ; very few results were available from the staffs of the factories. For the evaluation of domestic pollution, it was assumed that every house burned about 33 pounds of coal daily, the volatile sulphur in this being taken as about 1 per cent. The total number of houses was furnished by the local councils, so that approximate figures of SO_2 evolution could be arrived at ; however, these figures must be considered as minima, since the basic figures of 33 pounds and 1 per cent. sulphur are relatively low.

The chemists succeeded in fixing, among about thirty substances found to be polluting the atmosphere, the maximum concentrations reached by carbon monoxide, carbon dioxide, nitrous gases, sulphur dioxide, hydrofluoric acid. They concluded that the SO_2 evolved in the presence of oxidation catalysts, such as ferric and zinc oxide, in the fog, the SO_2 must have been partly transformed in sulphuric acid.[1]

The data thus collected and the toxicological analyses having been quite negative, the pathologists and industrial chemists sought to ascertain which of the thirty chemical substances left might have produced the medical symptoms described ; only those had to be considered which cause irritation of the respiratory or other mucous membranes. They therefore excluded the lack of oxygen and carbon dioxide, carbon monoxide and divers solid dusts, the latter because of unsuitable anatomical observations. They also excluded a series of noxious gases which could not have reached their threshold of toxicity, according to the balance established previously by the chemists, or because they would have brought on other symptoms or lesions than those pathologically observed.[2]

Very few substances remained. They must have been either in a gaseous state, or dissolved in very fine liquid or solid particles which might have adsorbed toxic gases. Among such substances, maybe SO_2 and its products of oxidation, HF, nitrous or ammoniacal vapours, HCl. Cold and dense fog could not of itself bring about death within the limits of the time observed, since the fog was just as opaque over all the east of Belgium, and should have brought about similar accidents, but this was not the case.

Now, neither nitrous vapours, nor ammoniacal vapours, nor hydrochloric acid had existed in the atmosphere in sufficient quantity to produce the accidents observed along the entire extent of the unfortunate valley, at every part of it, and at the same moment. Again, hydrofluoric acid had been emitted by one single chimney, located about the middle of the region in question, but this could not be responsible, since no signs of its diffusion in the atmosphere were noted when taking records of the precise moment when the first patients felt their first symptoms all along the valley ;

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[1] The fifteenth annual report of the investigation of atmospheric pollution for the year ended 31st March, 1929, said (page 2) : " A striking fact which emerged very early in the work was that in the place of experiment (Holborn) at all events, sulphur trioxide is not a normal constituent of the atmosphere ; it appears only during fog." This result was at the time " somewhat unexpected," to the British observers who had been accustomed for fifteen years to analyse the atmosphere.

[2] The following examples will give an idea of the interpretation given by the experts concerning the calculations of industrial chemistry.

Consider the possibility of a lack of oxygen in the air of the ·valley, due to surcharge of the atmosphere with large amounts of gases of combustion during the foggy days. An approximate idea of the maximal amount reached by these gases of combustion in the valley is ascertained as follows. The total volume of the valley is estimated at 3×10^9 cubic metres (about 30 km. long, 1 km. wide and 100 m. high). If the gases of combustion had completely surcharged this atmosphere, none being diffused outside, they would not, according to the chemical balance, have exceeded the following maxima : 42×10^6 cubic metres for CO_2, 10^6 for CO, 16×10^7 for nitrous gases, 10^5 for SO_2, i.e., a total of 2031×10^5 cubic metres. The oxygen contained in the air of the valley would not have decreased by more than 10 per cent., i.e., it would still have constituted at least 19 per cent. of the atmosphere, whilst it was long ago proved by Haldane and Smith that life is perfectly possible in an atmosphere containing only 15 per cent. and even less of oxygen.

Again, if all the CO_2 had remained in the valley during the fog (supposing, as is unlikely, that no diffusion was possible) the maximum increase in CO_2 for the entire volume of the valley would be less than 1·5 per cent.,whereas we know that man can live without discomfort in an atmosphere containing 2 per cent.

Moreover, the medical symptoms were not those usually observed in the case of need of oxygen, neither those of an intoxication by CO_2.

it could not, however, be absolutely excluded as a secondary factor acting in the near neighbourhood of the factory which issued it.

There then remained only SO_2, which issues in the largest abundance in the whole valley as a result of burning coal. It is moreover probable that part of the SO_2 (but it cannot be said, even approximately, how much) was oxidised into sulphuric acid, the threshold of toxicity of which is much lower. From the table, we can conclude that only the sulphur bodies have been spread in the whole valley, in amount sufficient to produce accidents among those exposed to the polluted atmosphere for several hours, while for all the other noxious gases, the amount established by calculation always remained far below the threshold of toxicity.

Sulphur dioxide probably existed in the air in amount insufficient to be noticed by its characteristic smell, but even in such small quantities, its toxicity for human beings may be very strong. It has been shown, *e.g.*, by Lehman and Hess that amounts of SO_2 from 170 to 640 mgs. per cubic metre and dissipated after half an hour or even one hour may be fairly harmless, although even as little as 20 mgs. per cubic metre may cause serious trouble after several hours.

Moreover, only from the action of sulphur pollution can we explain

CALCULATIONS ESTABLISHED FOR 25 KMS. (about 15 MILES) of the VALLEY, FROM HUY TO A POINT NEAR LIÉGE.

Name of Substance.	Rate of Toxicity after several Hours Exposure.	Maximum Amount which could have been reached after 1 Day of Fog.	Maximum Amount which could have been reached after 4 Days of Fog.
CO_2	+ 2 per cent. in volume	About 0·4 per cent. in volume	About 1½ per cent. in volume
CO	+ ½ f. 1000	About $\frac{1}{12}$ f. 1000	About ⅓ f. 1000
NO_2	12 to 16 cgs. for 1 m.³	1 to 2 mgs. f. 1 m.³	4 to 8 mgs. for 1 m.³
HF	Unknown; it must be about 4 mgs. for 1 m.³	0·08 mg. f. 1 m.³	0·3 mg. f. 1 m.³
SO_2	20 to 30 mgs. for 1 m.³	25 mgs. f. 1 m.³	100 mgs. f. 1 m.³
H_2SO_4	4 mgs. f. 1 m.³	38 mgs. f. 1 m.³ (Supposing the whole	152 mgs. f. 1 m.³ SO_2 would have been oxydated.)

why the accidents appeared simultaneously along the entire valley ; several hours of breathing such an atmosphere, where the noxious gases existed in relatively low amount, were necessary to provoke respiratory troubles. Several hours were also needed before the lower parts of the atmosphere, near the soil, were charged with sufficient quantities of sulphur bodies (mainly adsorbed on sooty particles ; the latter, issued from the high factory chimneys, could only reach the soil after several days). Moreover, a certain time had to elapse before the oxidation factors transforming SO_2 into SO_3 could act.

From the pathological standpoint, the two types of respiratory troubles noticed favour to a certain extent the idea that the noxious gases were sulphur dioxide and sulphuric acid. The physicians of the valley had all noticed, during the foggy days, (*a*) symptoms due to direct irritation of the mucous membranes with reflex symptoms (asthma and subsequent vascular collapse), certainly caused by a state of alcalosis in the blood, (*b*) on the other hand, symptoms of polypnaea with edema of the lungs, *i.e.*, action of noxious gases on the wall of pulmonary alveoli and very probably anoxaemia with acidosis of the blood. It is now well known [3] that irritant gases are

[3] Especially after the research of Henderson and Haggard.

mainly of two types according to the region of the respiratory ducts where they act : the soluble and dense vapours like H_2SO_4 in fine droplets will be fixed by the superior respiratory ducts, trachea or bronchi, while the lighter and less soluble gases, *i.e.*, SO_2 will penetrate into the deep cavities of the lungs and produce edema : in the first case, the clinical symptoms will be those of asthma ; in the second, those of anoxaemia with acidosis.

Finally, from the geographical distribution of the gravely attacked patients and the dead, one could see that the rate of SO_2 was higher at the extremity of the valley near Liége where factories and private houses are more numerous, than at the other end near Huy. The geographical conditions ot the valley above Liége are really very unusual and unfavourable when a weak easterly wind and fog appear together.[4]

In conclusion, we believe that undoubtedly the conjunction during more than three days of the same exceptional meteorological conditions would cause the same accidents if the industrial and domestic fires are equally active. Our measurements led us to the idea that one-fifth of the SO_2 issued in the valley came from domestic fires. Moreover, chemical analyses to control the pollution of the atmosphere in Liége itself (especially of sulphur bodies), showed that the latter reached a level in the city ten times higher than thirty years ago. The problems and the catastrophe here studied demonstrate once more the social and hygienic importance of questions connected with atmospheric pollution. In that field Great Britain is really the leading country.

Liége, 27th March.

[4] The extensive report of the question here summarised can be found in pages 260-335 of *Les problèmes de pollution de l'atmosphere*, by G. Batta, J. Firket and E. Leclerc. Edit. Georges Thone, Liége, and G. Masson, Paris, 1933 (462 pages).

GENERAL DISCUSSION.

Professor Firket in introducing his paper, referred to a scale map of the Meuse valley.

Mr. J. H. Coste (*Teddington*) said : The concentrations of sulphur compounds suggested by Firket as possible in the air of the Meuse valley during the fog in question are much greater than we have found in London under any weather conditions. Most people, it is supposed, can smell SO_2 when its concentration reaches 2 volumes per million, but it seems probable that sensitivity varies very much according to customary exposure ; a member of my family who has never lived in a large town can smell SO_2 in the white to pale yellow fogs we get in the semi-rural parts of the Thames valley, whilst town dwellers are probably less sensitive.

It seems probable that during bad fogs in industrial or crowded districts sulphuric acid is present in irritating amounts. In the fog of 23rd December, 1935, mentioned in my paper, the air, especially around the period of high SO_2 concentration was very irritant, affecting both the respiratory passages and the thin skin around the eyes. The effect was not unlike one's sensation when evaporating sulphuric acid in small quantities in a room.

In an industrial district there would always be enough nitrous acid in the air in still weather for appreciable oxidation of SO_2 to occur.

The evidence collected by the commission, which I read when the report was issued, was mainly circumstantial, but I think that an unusually big formation, with little dissipation, of sulphuric acid, was the most probable cause.

Dr. F. J. W. Whipple (*London*) said : The meteorological conditions described in Firket's paper are puzzling. It appears that there was

measurable wind throughout the period, and this seems at first sight in-consistent with the hypothesis that the air was practically stagnant in the valley. However, Firket has not given any information about the height of the Observatory where the wind was recorded, and it may be that the air current was persistent above the fog, which was confined to the valley. With a sharp inversion of temperature the upper air could glide over the top of the fog without dragging it along. It is perhaps important to notice that in a fog which is being cooled by radiation from the top and warmed by contact with the ground there is gentle convection and the temperature is nearly uniform. It is not justifiable to assume that smoke particles merely settle down through the fog, they are carried down by the convection currents.

It is difficult to believe that the deaths were due to breathing sulphur dioxide, since the conditions in the valley could hardly have been so bad as those which prevailed in the tunnels of the underground railway in London in the days of steam trains, where the sulphurous fumes were notorious, but conditions were not found unhealthy by the railwaymen. Is it not possible that some noxious product of the furnaces in the Meuse Valley has been overlooked ?

Dr. R. Lessing (*London*) said that he had directed attention to the emission of sulphur oxides in the combustion of fuels [1] six months before the Meuse tragedy. In a later paper,[2] he had shown that the annual emission of sulphur oxides in Greater London was, at a low estimate 500,000 tons in terms of H_2SO_4. The reason why free SO_3 or sulphuric acid was so rarely observed in the atmosphere was that it was readily neutralised by the lime or other basic dust always present in town air. During the first two or three days of the Meuse fog the lime particles settled out along with the soot and other solids so that later the sulphuric acid could not find neutralising material to act upon. Moreover, the high moisture saturation provided an ideal medium for the oxidation of SO_2 to SO_3 at a higher rate than in dry air.

Mr. G. Nonhebel (*Billingham*) (*communicated*) : The statements by Professor Firket that 20-30 mg. SO_2/M^3 and 4 mg. SO_3/M^3 air may cause trouble after several hours leads to the question : " What are the safe upper limits for the SO_2 and SO_3 concentrations in the lee of a large modern power station burning coal at a peak rate of several thousand tons per day." We have found that up to 10 per cent. of the sulphur in the gases from a powdered fuel plant may be present as SO_3.

Dr. S. R. Carter (*Birmingham*) said : Although excessive fog in the Meuse Valley is the subject under discussion, the reverse question interests me, as on the occasions when I have visited Liége the atmosphere seemed to be remarkably clear considering that it is a large manufacturing town. Is the reason for this known ?

[1] Second World Power Conference, Berlin, 1930.
[2] The National Smoke Abatement Conference, Bristol, 1935.

SULPHURIC ACID AS A DISPERSE PHASE IN TOWN AIR.

By J. H. Coste and G. B. Courtier.

The sulphur in air is mainly present as sulphur dioxide but under some atmospheric conditions it has been found that air from which the sulphur dioxide has been removed still shows measurable sulphur acidity. The acid constituent can be retained on a suitably fine filter, but experiments made with asbestos, sintered glass, and cotton wool filters confirmed our opinion that methods involving such filters are unsuitable when the acidity is of the low order found in the atmosphere. Apart from the small possibility that the filtering material may itself yield on extraction either alkali or acid to water, it is likely to separate from air all but the very finest suspended matter. This may, and probably does, include all or almost all the acid which is present in other forms than gas or vapour, but it will in most cases include particles which are either basic and when treated with water will yield a liquid of p_H greater than 7, or will easily be attacked by strong acids with the liberation of weaker ones, *e.g.*, carbonic or silicic acids.

We have, therefore, sought a means of separating free sulphuric acid from the air in which it may be present, without mixing it with the many other matters held in suspension in air. Since sulphuric acid is a very hygroscopic substance we have sought to take advantage of this fact by inducing condensation of water vapour by cooling, which should increase the mass of droplets of sulphuric acid or other hygroscopic nuclei so as to enable them to fall to the bottom of a vessel.

Experimental Methods.

Air which had been freed from sulphur dioxide was almost saturated with water vapour at room temperature and then passed through a flask immersed in ice. A condensate representing the greater part of the water content was obtained, which when sulphuric acid was found to be present, would have formed on nuclei of that compound in droplets sufficiently large to be retained in the flask. The condensate was almost free from dust and smoke particles, which passed through the flask and could be retained on a filter.

About 1000 litres of air were passed during 24 hours, yielding between 5 and 10 ml. of condensate. The p_H value was measured in the absence of carbon dioxide, and samples showing appreciable acidity were titrated with $N/250$ potash from a micro-burette using purified distilled water as the blank. In order to detect the presence of sulphates, 1 ml. of the condensate together with a drop of barium chloride solution was transferred to a watch glass and allowed to evaporate slowly on an electrically heated plate. Crystals of barium sulphate were observed, giving definite proof of sulphates in all samples showing acidity. Comparison with dilute standard solutions of sulphuric acid precipitated under the same conditions indicated that the acidity of the condensates could be attributed to sulphuric acid.

In the first experiments the compound of hydrogen peroxide and urea (Hyperol) was used for the absorption of sulphur dioxide. Hyperol is

more stable than free hydrogen peroxide in dilute solution and has a lower vapour pressure. Using a solution of about 1 per cent. in purified water and with two gas washers in series, it has been found, from extensive experience of sulphur determinations in air, that not less than 99 per cent. of the total absorption takes place in the first washer. Since this is true for the whole range of concentrations encountered, it can be assumed that with two washers gaseous absorption is virtually complete. Air passed through these washers yielded, on cooling, condensates with p_H values varying in different samples between 4·3 and 5·6. It was thought that there might be some possibility of sulphur dioxide being oxidised by hydrogen peroxide vapour in the gas phase with the formation of sulphuric acid, which would pass through the washers unabsorbed, and when deposited by water condensation might be considered as having been present in the air originally. Some further tests were therefore made using a solid absorbent having no appreciable vapour pressure. Broken pumice coated with lead peroxide, in U tubes, was found to be very efficient for the purpose, as air which had passed through these tubes yielded no acid to hyperol solution. When using lead peroxide for the preliminary removal of sulphur dioxide, the water vapour content of the air was raised nearly to saturation by passage through a wash tube, and when condensation was induced by cooling the water formed was found to be slightly acid as in the previous tests. The condensates obtained under these conditions had p_H values between 4·8 and 6·0. These values were rather higher than in the first series of tests but the difference can be attributed, at least in part, to the filtering action of the closely packed tubes.* Further evidence that the presence of sulphuric acid was independent of oxidation in the reaction tubes was obtained after using potassium hydroxide solution for the absorption of sulphur dioxide. A tube of pumice chips was inserted to prevent the passage of spray, and a p_H of 5·0 was measured.

A sensitive test for sulphurous acid is the change in blue shade produced n water slightly coloured by starch-iodine. When the condensates obtained by the above methods were tested with this reagent there was no evidence of the presence of sulphurous acid, although this was readily detected in samples resulting from the direct cooling of air without previous removal of sulphur dioxide. It was established that oxidation in such solutions was not rapid, and the absence of sulphurous acid in the condensates confirmed that the methods for preliminary removal of sulphur dioxide were adequate.

The " Monax " glass used for the apparatus, when thoroughly cleaned, was not appreciably affected by the solvent action of cold water having a p_H of the order encountered during the experiments.

Results.

The experiments were made, mainly in central London, under a variety of atmospheric conditions. The qualitative tests of the condensates obtained by the above methods consistently indicated the presence of traces of sulphuric acid, and the amounts were estimated to vary between 1 and 20 × 10^{-6} gm. per 1000 litres ; the sulphur dioxide in the same samples of air varying between 0·10 and 0·50 ml. (equivalent to 440 and 2200 × 10^{-6} gm. sulphuric acid). The maximum amounts of sulphuric acid were usually registered in periods of calm and in foggy conditions, while the amounts were invariably small after rain. No exact relationship was established but, in general, conditions which favoured high sulphur dioxide content also favoured high sulphuric acid content. There was some evidence that

* After the above was written, Mr. H. L. Wright found, in the course of further work with one of us on the nature of hygroscopic nuclei, that similar tubes packed with lead peroxide allowed only from 1/9 to 1/5 of the nuclei originally present in air to pass through, whilst the reduction in number of nuclei when air was passed through hyperol was of the order of 10 per cent.

the proportion of sulphuric acid was greater at ground level than at sixth floor level. Some observations made at an outlying northerly suburb showed that while the sulphur dioxide content was only 0·02 ml. per 1000 litres (equivalent to 44×10^{-6} gm. sulphuric acid) the amount of actual sulphuric acid was 4×10^{-6} gm.

From the experimental methods employed it may be concluded that the failure to retain the acid in the earlier absorbers with the gaseous sulphur dioxide was due to the existence of the sulphuric acid, probably associated with water, in aggregates of molecules—hygroscopic nuclei. Although the extraction of sulphuric acid in the condenser was not entirely complete, as was shown by the addition of an extra saturator and condenser, it did not appear that the total acid content was much greater than that stated.

Discussion.

The presence of such very small proportions of sulphuric acid in air containing relatively large proportions of sulphur dioxide may be explained on other grounds than the slowness of oxidation of the dioxide. When it is considered that facts point to the most obvious oxidising agent—nitrous acid—as occurring in air mainly in a liquid, or at least non-gaseous, phase,[1, 2] it appears that oxidation must be rather slow.

Sulphuric acid, as formed, will rapidly pass almost entirely into a liquid phase, although action occurring between sulphuric acid and a steam jet near which a drop of the strong acid is brought can only be explained by the concentrated acid having an appreciable vapour tension.[3]

N. Fuchs and N. Oschman[4] in attempting to form stable aerosols of sulphuric acid found difficulty in overcoming the tendency of droplets to combine to form larger ones. They succeeded, however, by rapid dilution of concentrated aerosols with relatively dry air, in obtaining uniform aerosols containing droplets estimated at $1·5 \times 10^{-6}$ cm. radius in relatively dry air, which is of the same order as that of the nuclei of Aitken[5] and the large ions of Langerin, which are considered as charged nuclei. A million of these per ml. of air would yield concentrations of H_2SO_4 of the order we have found. One of us and Wright[2] found that the rate of disappearance of nuclei obtained by burning fuel containing sulphur or by projecting SO_3 into air was very rapid, and this may be due as much to growth by absorption of water until the droplets are large enough to fall through the air with an appreciable velocity, as to recombination, although both these actions must go on. The tendency to form ammonium sulphate (ammonia is usually present in air), coalescence with heavy particles, including calcium carbonate (from building materials) and coke, must not be overlooked. Dusts collected in inhabited or industrial districts contain both alkaline and acid particles, these latter frequently being coke with an acid surface film, as shown under the microscope by the use of indicators. Frequently they contain sulphate.

The facts, generally, show that a considerable liquid phase of sulphuric acid droplets is very unlikely to occur in air; the conclusions,

[1] A. G. Francis and A. T. Parsons, *Analyst*, 1925, **50**, 262-72 ; G. Defren, *Chem. News*, 1896, **74**, 230-1, 240, 241 ; W. Hayhurst and J. V. Pring, *Trans. C. S.*, 1910, **97**, 868-77.

[2] J. H. Coste and H. L. Wright, *Phil. Mag.*, 1935, Sec. 7.20, 209-34.

[3] R. V. Helmholtz, *Ann. Physik u. Chem.*, 1887, **32**, 1-19.

[4] *Acta Physicochimica U.R.S.S.*, 1935, **3**, 61-78.

[5] J. J. and G. P. Thomson, *Conduction of Electricity through Gases*, 1928, 187-9.

based, it must be admitted, on circumstantial evidence of the Commission which reported on the Meuse Valley fog of 1st to 5th December, 1930, raise the strong presumption that when sulphuric acid becomes an important constituent of fog catastrophic disaster may be expected.

Summary.

A method of investigating the sulphuric acid content of the air has been devised, which does not involve the use of filters.   The free sulphuric acid content of London air has been shown to be of the order of 1 to 20×10^{-6} gm. per cubic metre.

This is of the order which would be expected having regard to the numbers of Aitken nuclei and the mass of sulphuric nuclei in artificially prepared aerosols of this acid.

Chemical Laboratory of the
   London County Council.

[6] *Bull. Acad. Roy. Med. Belg.*, 1931, 683-732.

GENERAL DISCUSSION.

Mr. C. F. Goodeve (*London*) expressed incomplete agreement with Coste and Courtier in the usefulness of the apparatus they described, and he did not agree that sintered glass filters are unsuitable.[1]   Such filters have been used to test the amount of sulphuric acid, in excess of the alkalinity, present in London's atmosphere on a number of occasions during January and February, 1934.   The extreme simplicity of the filter method over any other method makes it well worth considering carefully from the point of view of routine observations.   On the other hand the apparatus described by the authors requires careful watching and is slow with regard to the amount of air handled per hour.

It is agreed that the two methods might give slightly different results, but only if acid and alkaline particles exist independently in the atmosphere. There is no evidence at present to show whether or not this is the case, but the argument given in the paragraph below leads to the conclusion that it is unlikely.

Even if it is considered that the two methods do give different results, those obtained by the filter method would appear to have important practical advantages over those obtained by the method described by the authors.   The importance of knowing the sulphuric acid content of the air is largely due to its action on building materials and on living tissues. This action will be partly offset by the alkaline particles and therefore the *net* acidity is of importance.

The speaker called attention to the important observations of Ellis [2] who found that, even in the presence of high concentrations of a sulphur dioxide, the sulphuric acid content of London air was immeasurable, except in the presence of fog.   They found a maximum value of 0·62 volume parts per million (calculated as SO_2).   Some of the values obtained at University College during February, 1934, are shown in the table on next page.

The absence of sulphuric acid before fog particles are formed indicates that it cannot be considered as a *cause* of fog formation but rather as a contributing factor to the intensification of fog.   The amount of sulphuric

[1] The use of the sintered glass filters is discussed later, p. 1220.
[2] *The Investigation of Atmospheric Pollution*, Report on Observations, 1931, p. 38.

Date.	Volume of Air litres.	Time. Hours.	H₂SO₄ p.p.m. (vol.).	Remarks.
12/2/34	3440	7½	0·034	Slightly foggy.
14/2/34	2360	9½	0·019	Less ,,
15/2/34	3660	9¾	0·015	,, ,,
16/2/34	3580	9½	0·009	Fog in morning.
23/2/34	1390	7	0·0	Clear.

acid formed in flue gas is very small and the rate of oxidation in sulphur dioxide gas in the absence of liquid water is also small. Dr. Pinck (unpublished results) found that there was no oxidation in the presence of dry catalysts, such as iron oxides, even after a considerable period of time, but when water vapour was present sufficient to produce an adsorbed film over the catalyst, rapid oxidation at once took place. The formation of sulphuric acid in the atmosphere can take place by the condensation of water on nuclei (either alkaline or neutral), the subsequent solution of sulphur dioxide, and its rapid oxidation catalysed by the solid nuclei. If this is the case, there is no reason for the existence of independent alkaline particles in fogs and the two methods of analysis discussed above should give the same result.

Mr. J. H. Coste (*Teddington*), in reply, said : It is true, as pointed out by Mr. Goodeve that sintered glass is a good filtering medium for removal of dispersoids from air. In considering the useful work of Ellis (who used an asbestos filter as suggested to the Research Committee by Lambert of Oxford) I feel in the light of the certainty that acid and alkaline particles do exist together in air (a fact that Mr. Goodeve seems to doubt), that any method in which all the dispersoids are collected together is likely to yield erroneous results. Mr. Nonhebel has found that up to 10 per cent. of the sulphur in the gases from a powdered fuel plant may be present as SO₃, the amount of accompanying water vapour being great. This would go into the air as droplets, which would only be neutralised by collisions with alkaline particles or absorption of ammonia. Again, any sulphuric acid formed by the action of nitrous acid would be in droplet form, and neutralisation in free air would be much slower and less likely than when air was forced through a filter which was also separating alkaline particles.

The offsetting effect of alkaline particles can only come into play if acid and alkali are in juxtaposition. In collections of rainwater, containing the solids brought down with it, I have found alkaline zones surrounding particles in an acid liquid ; thus neutralisation does not always happen.

Mr. Goodeve's observations on fog are very interesting, and I agree with him that the presence of abundance of droplets of water with an accumulation of sulphur dioxide (and nitrous acid) which would occur in a town fog is likely to raise the sulphuric acid content from an infinitesimal to a measurable amount.

THE INFLUENCE OF URBAN CONDITIONS ON THE CIRCULATION OF ELECTRICITY THROUGH THE ATMOSPHERE.

By F. J. W. Whipple.

Atmospheric electricity is a subject in which it is difficult to disentangle the influence of world-wide forces and of local conditions. In every situation there are a number of phenomena to be observed and correlated, and at present there is no observatory which can claim that all the relevant measurements are being made regularly, or even intermittently. Of the elements which can be recorded, potential gradient is by far the most frequently observed, but the interpretation of the changes in the value of this element is now known to be very complicated.

It has been realised for a long while that the fact that there is a gradient of potential is evidence for the existence of a charge on the ground, and of a complementary charge in the atmosphere. Normally the ground carries a negative charge, and the complementary charge is positive. Observations in balloons indicate that the potential gradient falls off rapidly with increasing height, so that the charge in the atmosphere is mostly at low levels. One way of regarding observations of potential gradient is that they are measurements of the space-charge in columns of the atmosphere.

Alternatively, attention may be concentrated on the flow of electricity. Owing to ionisation, the air is a conductor, and under the influence of potential gradient a current flows from the upper air to the ground. In a steady state the current must be the same at all heights. This rule is in accordance with observation, *i.e.* in individual ascents the product of potential gradient and conductivity has been found to be constant, as nearly as can be expected from the circumstances of the observations.

A fundamental problem in Atmospheric Electricity is to explain how this air-earth current, which prevails in fine weather in all parts of the world, is maintained. It is known that in the upper atmosphere there are layers of highly ionised air, of which the most important from the present point of view is the Kennelly-Heaviside layer at a height of about 100 km. The conductivity of this layer is so good that it must be at very nearly the same potential over all parts of the world.

If electricity flows downwards from the Kennelly-Heaviside layer in regions where there is fine weather, the supply must be maintained by upward currents predominating in regions where there is bad weather.

In fact, rain-clouds act as electrical machines pumping electricity up towards the K.-H. layer. Wormell has shown that the available estimates of the quantity of electricity exchanged between clouds and ground by conduction currents, by charged rain and by lightning are consistent with this hypothesis, which, it may be noted, does not involve any particular theory of the mechanism by which the separation of electricity in the clouds is produced.

The potential of the K.-H. layer being the same in all parts of the

globe, the current which flows towards the ground in any place must depend on the conductivity of the air, the current varying inversely as the effective resistance of the column of air between the ground and the Heaviside layer. The electricity is carried by ions, positive ions moving downwards and negative ions upwards ; it is only by the current of positive ions that electricity is communicated to the ground, so that the strength of the air-earth current is proportional to the potential gradient and to the conductivity due to positive ions. This may be expressed otherwise by saying that the potential gradient is proportional to the current, and to the specific resistance of the air.

DIURNAL VARIATION IN
SUMMER.
Fig. 1.
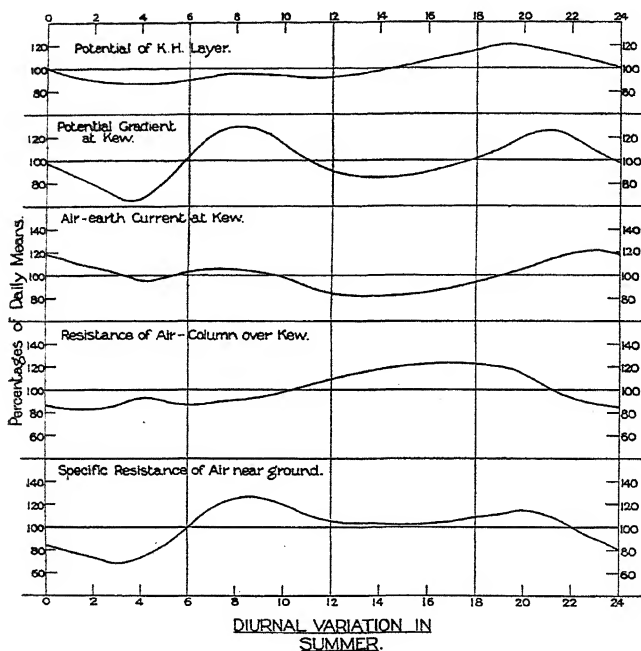
It will be seen that, according to the theory which has been sketched, the potential gradient at any time and place is

(a) proportional to the potential of the K.-H. layer ;
(b) inversely proportional to the effective resistance of a column of the atmosphere ;
(c) proportional to the specific resistance of the air near the ground for positive electricity.

It is proposed to apply this theory to the interpretation of observations of the diurnal variation of potential gradient at Kew Observatory. For this purpose, we shall consider the diurnal variation during four summer months and four winter months in 1930 and 1931, during which there were continuous records [1] of the air-earth current at the Observatory.

[1] F. J. Scrase, " The Air-earth Current at Kew Observatory," *London Met. Office Geophysical Memoirs*, No. 58 (1933).

Fortunately, these short periods yielded diurnal variation curves which were true to type. These are shown in the second lines of Figs. 1 and 2. Both in summer and in winter there are two maxima and two minima in the course of the day.

The uppermost curves in the diagrams represent the diurnal variation of the potential of the Heaviside layer. These curves are not as speculative as might be supposed. It will be noticed that the absolute value of the potential is not involved, we are only concerned for the moment with proportional changes. Now, it will be realised that over the oceans there is no pollution, and no considerable systematic variation in temperature, so it may be assumed that at points far from land the total resistance of a column of the atmosphere is constant throughout the day,

DIURNAL VARIATION IN
WINTER.
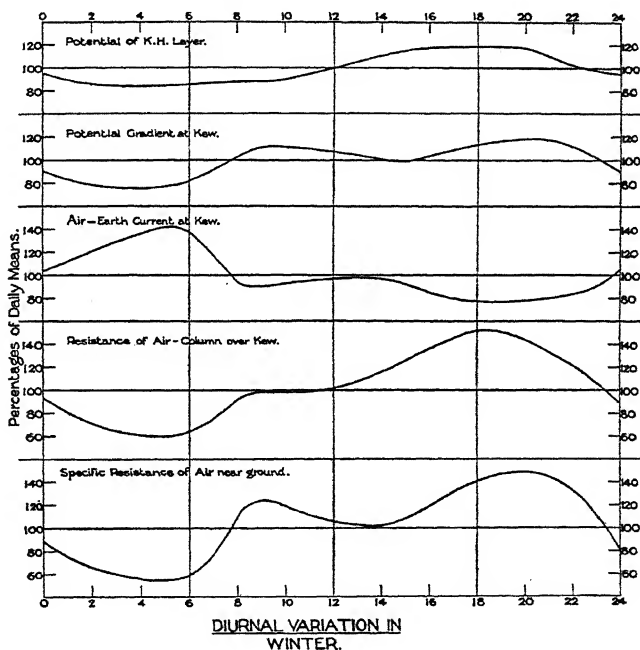
FIG. 2.

and also the specific resistance of the air in the lowest layer. Accordingly, the changes in potential gradient are proportional to the changes in potential of the Heaviside layer. Now, it was established by Mauchly that the changes in potential gradient over the oceans depended on Greenwich time, not local time, and this is confirmation of our hypothesis. The curves to which reference has been made are derived [2] from the observations of potential gradient over the oceans; the curve used for comparison with the Kew potential gradient on summer depends on observations during the months May to October, and that for comparison with the Kew gradient in winter on observations during the

[2] Whipple, *Q.J.R. Met. Soc.*, 1929, **55**, 9.

months November to April but the difference in type is slight, so that no serious error can be introduced by this selection of months.

The curves indicate that the potential of the K.-H. layer is lowest about 4 h. G.M.T., and highest about 19 h. G.M.T. As was first noticed by Appleton, this is consistent with the ideas that the potential is maintained by the action of thunderstorms, that in any place on land thunderstorms are most likely in the late afternoon, and that the most thundery regions are in Africa and South America.

The next step is to consider the observations of the air-earth current at Kew. As will be seen from the curves in Figs. 1 and 2, the types of variation of the current in summer and winter are very different. In summer the current behaves in much the same way as the potential gradient at the same station, in winter there is a reversal.

Regarding the current as produced by the potential of the K.-H. layer, we investigate the changes in the resistance of a vertical column by dividing the potential by the current. We learn in this way that the resistance is least in the early morning, and increases fairly steadily through the day, the maximum being reached about 18 h.

The specific resistance of the air in contact with the ground is found in the same way by comparing the potential gradient at Kew with the air-earth current. The specific resistance has two maxima and two minima in the twenty-four hours.

Thus it appears that the morning minimum and the evening maximum of potential gradient at Kew are due in part to the corresponding extremes of the potential of the K.-H. layer, but the morning maximum and the evening minimum are due entirely to local conditions.

At the time of the morning maximum of potential gradient the specific resistance near the ground is high, whilst the total resistance is low (in summer) or moderate (in winter). At the time of the afternoon minimum of potential gradient the specific resistance is moderate, whilst the total resistance is above the mean for the day. To explain the variations in the total resistance, we notice that the conductivity of the air depends on the number of small ions which it contains. The number of small ions depends on the rate at which ions are produced, and on the rate at which the lives of the small ions are terminated by their combination with nuclei, charged and uncharged. We do not know whether the rate of production fluctuates through the day at moderate heights in the atmosphere, but we do know that the number of nuclei will increase owing to the way they are steadily produced by fires and by the use of gas. According to the work [3] of Coste and Wright, nuclei are mostly nitrous acid HNO_2 formed by the combination of the atmospheric gases nitrogen, oxygen and water vapour and therefore nuclei can hardly be regarded as pollution. They are produced, however, at the same time as the sooty particles which are pre-eminently pollution. The way in which the total resistance changes indicates that over a London suburb the number of nuclei increases steadily from the time when fires are lit in the morning until about 18 h. in the evening, and that the air clears gradually during the night. It is probable that at night in summer the nuclei are mostly sea-salt, as they are at all times over the oceans.

The double oscillation in the specific resistance of the air near the ground has been explained by Simpson. There is a rapid increase in the

[3] *Phil. Mag.*, 1935, 7, 20, 209.

resistance in the morning, but this increase is interrupted when the sun is up and the warming of the ground produces convection currents which carry pollution and nuclei upwards and allow purer air to descend. Convection becomes less vigorous in the late afternoon, and pollution increases to reach a maximum in the evening when domestic fires and domestic cooking-stoves are still active. The evening maximum is a little later in winter than in summer.

In this discussion we have dealt only with the proportional variation of the elements concerned. In considering the mean values, we are handicapped by not knowing at all precisely the mean value of the potential of the Heaviside layer at different seasons. There is reason to believe that the potential is higher in the northern winter than in the northern summer, for it is found both in the Arctic and in the Antarctic that potential gradient is higher in the former season, and the same relation has been observed over the oceans. On the other hand Mauchly's final analysis[4] of the Carnegie observations of potential gradient indicates no appreciable annual variation over the oceans. Balloon observations of potential gradient lead to an estimate of about $2 \cdot 5 \times 10^5$ volts for potential at 10 km. Above that level the gradient is very small. We take 3×10^5 volts for the potential of the Heaviside layer at all seasons.

The best estimate of the air-earth current over the oceans can be obtained from the mean potential gradient and the conductivity due to position ions and is

$$1 \cdot 3 \times 1 \cdot 8 \times 10^{-16} = 2 \cdot 3 \times 10^{-16} \text{ amp./cm}^2.$$

The following Table is completed[5] by taking Scrase's estimates of the potential gradient and air-earth current at Kew.

MEAN VALUES.

	Oceans.	Kew Observatory.	
		Summer.	Winter.
Potential of the Heaviside layer	3	3	3×10^5 volts.
Potential gradient	1·3	2·46	4·70 volt/cm.
Air-earth current	2·3	1·48	$\cdot 74 \times 10^{-16}$ amp./cm.^{2}
Effective resistance of air column	1·3	2·0	$4 \cdot 0 \times 10^{21}$ ohm. cm.^{2}
Specific resistance ($+$ ions)	0·56	1·66	$6 \cdot 35 \times 10^{16}$ ohm. cm.
Conductivity ($+$ ions)	1·8	·60	$\cdot 16 \times 10^{-16}$ ohm.$^{-1}$cm^{-1}
Conductivity in electrostatic units	1·6	·54	$\cdot 14 \times 10^{-4}$ sec.$^{-1}$

It will be noticed that whereas the specific resistance at Kew is increased fourfold between summer and winter, the total resistance of the air-column is only doubled.

The minimum resistance, at 5 h., in winter, is nearly equal to the maximum resistance, at 18 h., in summer. Further, the winter maximum,

[4] *Carnegie Inst. Dep. Terr. Magn., Washington,* 1926, **5,** 403.
[5] *Loc. cit.* Tables IV. and II. It is to be noted that an exposure factor has to be applied to the data in these Tables. The conductivity is derived here from seasonal means of current and potential gradient, whereas in Scrase's Table III. the values of conductivity for the months were averaged.

at 19 h., is about 6×10^{21} ohm. cm.², whereas the summer minimum, at 2 h., is only $1\cdot4 \times 10^{21}$ ohm. cm.², almost the same as the resistance over the oceans. Here, again, we have a fourfold increase.

So far, we have been concerned with the variation of the effective resistance of an air column. This effective resistance is virtually defined by the equation

$$V = iR,$$

V being the voltage at the top of the column, and i the air-earth current, and it is important to notice that R is not the same as r, the integral of the specific resistance at all heights. This integral is defined by

$$\cdot = \int_0^h \frac{\iota}{\lambda_1}.$$

in which λ_1 and λ_2 are the conductivities due to positive and negative ions respectively, and h is the height of the column. That R and r are not the same, is on account of the " electrode effect." Owing to the fact that negative ions cannot pass upwards from the ground itself, the current at the surface is conveyed only by positive ions. At a moderate distance from the ground there is an excess of positive charge, and in addition to the conduction current there is a diffusion current carrying positive electricity upwards. Above the region in which the " electrode effect " is appreciable the potential gradient is related to the conductivity by the equation

$$\partial z$$

whereas at the surface

$$\partial V \qquad \frac{i}{\lambda_1}.$$

To allow for the transition, which must be gradual, we may adopt the hypothesis that at any height the gradient is given with sufficient accuracy by the formula

$$\partial V \qquad i$$

a being a constant and c the value of $\lambda_2/[\lambda_1(\lambda_1 + \lambda_2)]$ near the ground. This formula, which reduces to the two preceding ones if $z \rightarrow \infty$ and if $z \rightarrow 0$ respectively, does not imply that the λ's are constant. By integrating the last equation, we find that

$$R = r + ac.$$

By adopting a simplified theory concerning the nature of the electrode effect, I calculated that the value of a would be of the order 30 metres. In this calculation,[6] it was assumed that λ_1 and λ_2 were independent of height, and that the coefficient of eddy-diffusion was also constant. It is known, however, from experiments at Kew that at that station, at any rate in the middle of the day, the potential gradient is nearly the same at 10 metres and at the ground. If our method of approximation to the value of $\frac{\partial V}{\partial z}$ is valid, then a must be considerably greater than 30 metres. Let us suppose that $a = 100$ metres, then with the average

⁶ *Terr. Mag.*, 1932, **37**, 355.

summer values of the conductivities c is about 0.7×10^{16} ohm. cm., and $ac = 0.7 \times 10^{20}$ ohm. cm. As R in the same season is about 2×10^{21} ohm. cm., r is then about 3 per cent. less than R.

In winter there is generally less diffusion by eddy motion, and it may be surmised that $a = 50$ metres. In this season the average value of c is about 2.5×10^{20} ohm. cm., so that, according to our surmise, $ac = 1.25 \times 10^{20}$ ohm. cm. With R at the average winter value, 4×10^{21} ohm. cm. r is again 3 per cent. less than R.

As to diurnal variation of ac, it is to be noticed that when the air is stable at night, a is likely to be small as well as c, so that the product ac is small then; in the morning c increases before there is much convection; later in the day, c decreases and convection increases; there is therefore not much to guide us in deciding at what hour ac is likely to have its maximum value. It may be that ac, like R, increases through the daylight hours. There is no reason to suppose that the difference between R and r is at any time much greater than the 3 per cent. which has been estimated as the average proportion, but it may well be that the difference can reach, say, 10 per cent. In that case, a considerable part of the regular diurnal change of R must be ascribed to the varying vertical extent of the electrode effect. In using the generalisation which has been put forward, that the resistance of the atmosphere increases throughout the hours when pollution is occurring, it must be borne in mind that the generalisation refers to the effective resistance R, and not to the true electrical resistance r. Whether r really behaves in the same way must be left undetermined.

This discussion is, it must be admitted, rather inconclusive. It may serve, however, to draw the attention of physicists to the difficulty of interpreting such simple observations as those of potential gradient. Systematic observations of what was then called electric tension were commenced at Kew Observatory in 1843. We are still a long way from fully understanding their significance.

Kew Observatory.

ON SULPHURIC ACID MIST.

BY A. DOOLEY AND C. F. GOODEVE.

Sulphur trioxide vapour, when passed in an air stream through water, is not appreciably absorbed, but is converted into a mist which is stable to acids and alkalies. On the other hand, when the vapour is passed through 98 per cent. sulphuric acid, it is practically completely absorbed. A number of theories have been suggested to explain this behaviour; for example, Sackur[1] thought that the sulphur trioxide was converted into an insoluble form, S_2O_6.[2] A more acceptable explanation was put forward by Walker, Lewis and McAdams,[3] who state that:

[1] O. Sackur, *Z. Elektrochem.*, 1902, **8**, 77.
[2] I. E. Adadurov and D. V. Gernet, *J. Chem. Ind. Russ.*, 1931, **8**, No. 18, p. 12, hold somewhat similar ideas.
[3] W. H. Walker, W. K. Lewis and W. H. McAdams, *Principles of Chemical Engineering*, 1923, p. 42.

" If one attempts to dissolve the trioxide in water or dilute sulphuric acid, the trioxide vapour first comes in contact not with the liquid but with the water vapour which has evaporated from the liquid into the gas. It reacts with this vapour, producing minute droplets of sulphuric acid in the form of a fog, and these droplets are effectively insulated from the absorbing liquid by the gas film. One must therefore use as an absorbent (for the trioxide) [4] a liquid, the water vapour pressure of which is negligible, *i.e.*, strong sulphuric acid. This is the reason why for absorption one must use acid between 97 and 98 per cent. If more dilute, the pressure of water vapour is sufficient to produce a fog, if more concentrated the partial pressure of SO_3 over it is great enough to prevent complete absorption."

Recent experimental evidence strongly supports this latter explanation, and makes it possible to account more fully for the formation of sulphuric acid mist, and its various properties. In the first part of this paper, the whole mechanism is discussed, and in the second, the equilibria that obtain under various conditions have been calculated.

In problems dealing with sulphuric acid, it is very important to distinguish, as has been done by Miles,[5] between the absorption of sulphur trioxide vapour and the removal of sulphuric acid mist. These problems are quite separate, and their solutions generally lie in different directions.

The Formation of Sulphuric Acid Mist.

Goodeve, Eastman and Dooley [6] have recently studied the kinetics of the reaction between sulphur trioxide and water vapours. It was found that the primary reaction

$$H_2O \text{ (vapour)} + SO_3 \text{ (vapour)} \rightarrow H_2SO_4 \text{ (vapour)}$$
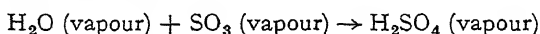
was approximately stoichiometric and very fast. Under the conditions described (*i.e.*, at low pressures of reactants and a carrier gas pressure of about 5 mm.) about 1 collision in 100 between reacting gas molecules was found to be effective. This velocity corresponded approximately to the rate of termolecular collisions. It would probably, therefore, increase as the first power of the concentration of each of the reactants and of the pressure of the carrier gas. The fact that the reaction was not altered by careful purification of the gas to remove all particles of dust, led to the conclusion that the reaction was mainly homogeneous. These characteristics of the reaction resulted in a very narrow reaction zone, whose position was determined by the relative concentrations of the reactants and the diffusion velocities. The stoichiometric character of the reaction required that the rate of arrival of each of the reactants in the reaction zone should be the same, and, if the concentration or flow rate were altered, the zone would change its position until these conditions were fulfilled.*

The rate of arrival of water vapour at the reaction zone is a function of the concentration gradient which, in turn, depends on the rate of evaporation of water from a liquid surface. This latter problem has

[4] The words in brackets are the authors.
[5] F. D. Miles, *Manufacture of Sulphuric Acid (Contact Process)*, 1925, p. 209.
[6] C. F. Goodeve, A. S. Eastman and A. Dooley, *Trans. Faraday Soc.*, 1934, 30, p. 1127.
* See Fig. 2, previous paper.

been studied recently by Alty and co-workers,[7] who find that the rate of evaporation is approximately one-thirtieth of the rate of surface collisions for the saturated vapour. On the other hand, they find that the accommodation coefficient for transfer of energy of collisions of water molecules with a water surface, is unity. The accuracy of their experiments was not high, owing to necessary extrapolations, and it would appear that the value $(\frac{1}{30})$ for their first coefficient represents a minimum. The rate of evaporation of water into a vapour whose pressure is 1 mm. below the equilibrium pressure can, therefore, be calculated to be at least 2×10^{19} molecules per second per sq. cm. Unless the rate of arrival of sulphur trioxide is greater than this, the water surface will always be protected by a layer of water vapour.

This forms a starting point for the development of a three-stage mechanism of mist formation. The high velocity of the reaction producing molecular hydrogen sulphate does not permit the sulphur trioxide, as such, to reach the water surface. This hydrogen sulphate will be in a state of supersaturation and its concentration will increase until it reaches a critical value, whereupon condensation will occur with the production of agglomerates or nuclei of hydrogen sulphate. This is the second stage. The delay which occurs in reaching this critical point gives rise to the periodic phenomenon described in the previous paper. A few molecules of hydrogen sulphate will, however, penetrate the protecting water layer and enter the liquid water. The number that do this will depend chiefly on the distance between the reaction zone and the water surface.

The concept of the formation of nuclei of an involatile material as a necessary preliminary to the formation of a mist has been advanced by Townsend,[8] and supported by Rothmund [9] with regard to mists of sulphuric acid and iodic acid, and by Philip and co-workers [10, 11] with respect to mists of hydrogen chloride.

The average number of molecules in these nuclei depends upon a number of conditions as yet not fully understood. This number may depend on the rate of condensation as normally controlled by the partial pressures, the number of foreign nuclei such as dust or ions, the rate of cooling of the carrier gas,[12] etc. Some important factors affecting its value are discussed by Freundlich.[13] In addition, a theory based on initial aggregation of molecules has been proposed by Volmer.[14] A theory of this type is favoured here, as it gives a simpler explanation of the delay in precipitation found in the periodic phenomenon. The size of the nuclei is of major importance in determining the equilibrium conditions of the mist, as will be discussed below.

The third and final stage in the process occurs when the agglomerates of hydrogen sulphate are carried by the air stream into a part containing excess of one or other of the reactants. This is absorbed until equilibrium is attained, resulting in the production of particles of strong light-scattering power which form the well-known sulphuric acid mist.

[7] T. Alty and F. H. Nicoll, *Canad. J. Res.*, 1931, **4**, 547 ; T. Atly and C. A. Mackay, *Proc. Roy. Soc.*, 1935, **149A**, 104.
[8] J. S. Townsend, *Proc. Camb. Phil. Soc.*, 1900, **10**, 52.
[9] V. Rothmund, *Z. Elektrochemie*, 1917, **23**, 170.
[10] R. W. Aldis and J. C. Philip, *J.C.S.*, 1930, p. 1103.
[11] C. N. Jackson and J. C. Philip, *J.C.S.*, 1934, p. 341.
[12] See B.P. 429,267 to Metallges, A. G.
[13] H. Freundlich, *Colloid and Capillary Chemistry*, 1926, p. 769.
[14] M. Volmer, *Z. Elektrochem.*, 1929, **35**, 555.

The two types of mist described by Remy,[15] and called " wet " and " dry " mists, correspond to the cases where the hydrogen sulphate nuclei pass into an atmosphere containing excess water vapour and excess sulphur trioxide, respectively. " Wet " mist consists, therefore, of droplets of sulphuric acid in various stages of dilution, and the " dry " mist, of droplets of oleum. Although these two mists are different as regards composition and some properties, their modes of formation are strictly analogous. For example, the periodic phenomena could be produced in an identical manner simply by reversing the relative concentrations of reactants.

The above mechanism has been demonstrated by a simple experiment in which air-sulphur trioxide mixtures were passed into a tube in which was placed a drop of water, as shown in Fig. 1. The clear space between the reaction zone and the liquid water was readily visible, as was also the carrying away in a thin layer of the sulphuric acid mist from the water. The drop was found to evaporate rapidly. Generally, however, the drop did not evaporate completely as some sulphuric acid diffused through to the water, was dissolved and lowered the vapour pressure of the water. This lowering resulted in an approach of the reaction zone and a still greater penetration of the sulphuric acid. Eventually, the whole system ceased to produce mists in the tube.
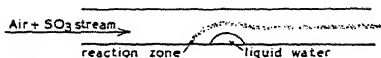
Fig. 1.

As was to be expected, the same phenomenon could be demonstrated by having water vapour in the air stream and a drop of strong oleum (about 50 per cent. free SO_3) in the tube.

The efficiency of removal of *sulphur trioxide* from an air stream is, according to the above mechanism, almost entirely dependent on the lowness of the vapour pressure with respect to SO_3 or H_2O. The importance of low partial vapour pressures of the absorbing medium has often been emphasised. Miles [16] has shown by a series of experiments that the efficiency of absorption increases very rapidly with decrease of temperature. In the design of commercial plant, special precautions are taken, as described by Fairlie,[17] to ensure that the final absorption is done with cold acid.

Presumably a solution of any non-volatile substance which will reduce the vapour pressure of water to a very low value could be used as an absorbing medium—that is, the power of absorption may not be specific to sulphuric acid.

The Stability of Sulphuric Acid Mist.

The stability of mists to alkalies, etc., has at times been attributed to adsorbed air films, electrical charges, etc.[18] The existence of strongly adsorbed air films at liquid surfaces has not been proved, and is not to be expected, the low solubility of air in liquids indicating a low attraction between air molecules and liquids. Air cushions between colliding droplets of reasonable size are well known, but their effect in preventing contact on collision decreases very rapidly with decrease in droplet size.

[15] H. Remy, *Z. Elektrochem.*, 1922, **28**, 467.
[16] F. D. Miles, *loc. cit.*, p. 250.
[17] A. M. Fairlie, *Sulphuric Acid Manufacture*, 1936.
[18] See W. E. Gibbs, *Clouds and Smokes*, 1924, p. 96.

A thermodynamic metastability of aerosols due to adsorbed electric charges of one sign, as occurs with ordinary liquid colloids, is not possible in a medium of very low dielectric constant. In addition, Remy and Koch [19] found that mist particles of sulphuric acid were uncharged.

The whole subject of the stability of aerosols has been made clear by the work of Tuovila and of Whytlaw-Gray and collaborators.[20] It has been found for stearic acid that every collision between mist particles results in their coalescence, and that the so-called stability can be entirely accounted for by the low diffusion velocity and low collision frequency of the particles. This indicates that adsorbed air films and electric charges, if present, were without effect.

Although no quantitative experiments have been performed for sulphuric acid mist, there is no reason to doubt that the same conditions apply, and therefore we can assume that the " resistance " of sulphuric acid mist to scrubbing agents is simply an indication of the low diffusion velocity.

Equilibrium Conditions for Sulphuric Acid Mist.

Although the stability of mists with time is only an apparent one, the particles themselves come into true thermodynamic equilibrium with the reactant vapour which happens to be in excess. The case in which water vapour is in excess is considered in the following. It is possible to obtain an equilibrium even when the partial pressure of water is equal to that over a pure water surface. Townsend [8] derived an expression for the radius of a droplet in a water-saturated atmosphere, in terms of the osmotic pressure " of the soluble body." He equated the increase in vapour pressure due to curvature, as given by the Kelvin equation, to the lowering of vapour pressure of water corresponding to the osmotic pressure. Rothmund [9] obtained a similar expression,[21] using Raoult's law and the Van t'Hoff factor i. For an iodic acid mist, he found agreement between values for the radius so obtained, and as calculated from the rate of fall using the Stokes-Cunningham relationship. These equations can only be used for large particles where the approximations are valid, and for droplets in equilibrium with saturated water vapour. Under conditions other than these, as is shown below, the equilibrium radius is practically independent of concentration, except for droplets containing a given number of sulphuric acid molecules.

In order to follow the increase or decrease of size of a mist particle resulting from a change in the vapour pressure, it is necessary to proceed in another way. For a given droplet, the one important quantity which does not vary is the content of hydrogen sulphate, $i.e.$, the size of the initial nucleus. This may, however, vary considerably for droplets formed under various conditions. The variables concerned are inter-dependent, and this inter-dependence is not of a simple form. It is not useful to attempt a single equation to express the conditions obtaining in sulphuric acid mist. It is, however, possible to construct a series of curves showing the growth of droplets of sulphuric acid mist derived from

[19] H. Remy and C. Koch, $Z.$ $anorg.$ $Chem.,$ 1924, **139**, 69.

[20] This question has been fully discussed in $Smoke$ (1932), by Whytlaw-Gray and Patterson.

[21] Care should be observed in using Rothmund's equations, as he has omitted the density in two of them. His last equation is correct as the density would have cancelled out.

hydrogen sulphate nuclei of various sizes in the presence of water vapour at various pressures.

The Kelvin equation for variation of vapour pressure with curvature is derived thermodynamically [22] in, for example, Guggenheim's *Modern Thermodynamics*.[23] This equation may be written—

$$P$$

(1)

where R is the gas constant, T the absolute temperature, P and P_0 the vapour pressures over the droplet and corresponding plane surface respectively for the same strength of solution, γ the surface tension, $\dfrac{dv}{dn}$ the partial molar volume and r the radius. The quantities P_0, γ and $\dfrac{dv}{dn}$ are all functions of concentration, and these functions can only be expressed in the form of experimentally determined curves. These have been drawn in Fig. 2, the temperature throughout being 20° C. The values of P_0 were taken from the International Critical Tables,[24] of γ from the results of Linebarger [25] (corrected for the now accepted value for water), and of $\dfrac{dv}{dn}$ from the specific volume-concentration curve by the method of intercepts.[26] In obtaining Fig. 2, the values of the concentration in grams H_2SO_4 per c.c., were first plotted against $\log_{10} \dfrac{r}{r_0}$ (where r_0 is the radius of the initial nucleus of hydrogen sulphate), a purely geometrical calculation. Values of the other variables were then plotted through this concentration on the $\log_{10} \dfrac{r_0}{r}$ scale. All of the essential data are shown in this figure.

Fig. 2. Physical Properties of Sulphuric Acid as used in equation I.

The quantities γ and $\dfrac{dv}{dn}$ are also functions of the radius. The amount of the correction for change of surface tension with curvature has apparently not been calculated, but would be of minor importance at diameters above 10^{-6} cm.—that is, where the curvature is small compared with that of the molecules. The correction for variation of partial

[22] A number of kinetic derivations have also been made. For example, see S. W. Gorbatschew, *Kolloid Z.*, 1935, **73**, 263.
[23] E. A. Guggenheim, *Modern Thermodynamics*, 1933, p. 170.
[24] Vol. III., p. 302.
[25] C. E. Linebarger, *J.A.C.S.*, 1900, **22**, 5.
[26] Lewis and Randall, *Thermodynamics*, p. 38.

molar volume with curvature [27] is also very small, and most likely much less important than the change of surface tension. These corrections will be neglected here as we are generally dealing with droplets of sufficient size to give a strong Tyndall beam—*i.e.*, greater than 10^{-6} cm. The effect of electrical charges is also not considered.[28]

Values for the equilibrium pressure P, over droplets of radius r, arising out of an initial nucleus of hydrogen sulphate of radius r_0, have been calculated for a series of selected values of the latter, using Equation (1). The resultant members of a family of curves are shown in Fig. 3, the equilibrium vapour pressure being plotted against the logarithm of the droplet radius. The curves trace the history of the growth of the sulphuric acid droplets, excluding coagulation by collision, and show the equilibrium size to be expected when the droplets are carried in a gas containing water vapour at various partial pressures. When air carrying droplets of sulphuric acid mist is passed through liquid water, it becomes
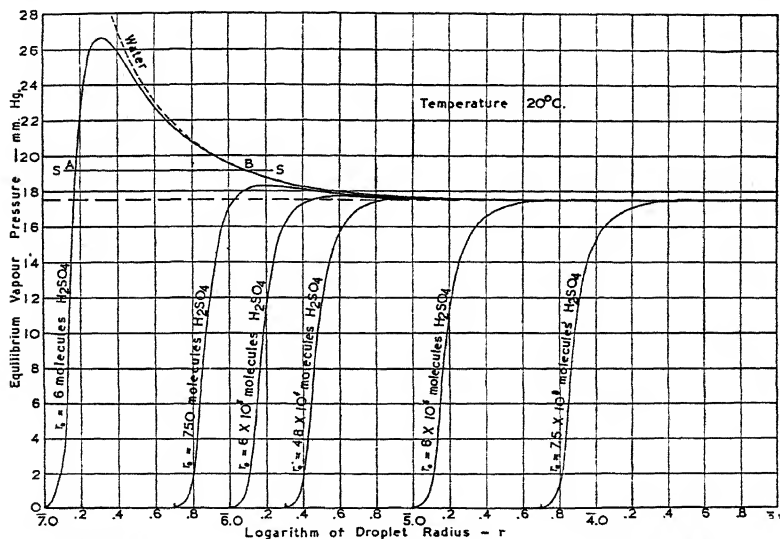
Fig.3. The Growth of Sulphuric Acid Mist Droplets from Hydrogen Sulphate Nuclei of Radius r_0.

saturated with water vapour to a partial pressure, as indicated by the horizontal broken line. Water vapour will condense on the mist particles until their radius is raised to the value given by the point where the curve crosses this horizontal line. The parts of the curves above this line represent an unstable state, and the droplets will lose water until they reach the equilibrium radius. The rate of evaporation of water from such droplets will be a function of the distance from the

[27] Kritschevski, *Kolloid Z.*, 1934, 68, 15, has calculated a correction for change of volume with curvature, based upon an equation taken from Lewis and Randall (*loc cit.*, p. 252). However, he has apparently confused partial molal volume and total volume. At all events, the equation given by Lewis and Randall cannot be accepted if for no other reason than the fact that it is derived from the variation of free energy for a change in a system which cannot possibly be considered as reversible.

[28] The effect of charges has been calculated by J. J. Thomson, *Conduction of Electricity through Gases*, 1928, Vol. I., p. 325 *et seq.*

appropriate point on the curve to the horizontal line, and will pass through a maximum as a large drop evaporates.

A similar set of curves may be plotted for the case of H_2SO_4 nuclei in an atmosphere containing gaseous SO_3. The vapour pressure of SO_3 over the various strengths of oleum would then be represented by P_0, and the other physical properties of this material would be used where required. These curves would be useful in considering the general properties of oleum mists.

A comparison of Fig. 3 with Fig. 2 will show that the variation of vapour pressure with concentration is the major factor in determining the equilibrium pressure of the drop. The concentration does not depend markedly upon radius for a given partial pressure, and a determination of concentration cannot readily be used to determine the size of the droplets. A heterogeneous mist containing particles whose sizes are spread over a wide range will give effectively the same value for concentration as a homogeneous mist, so long as none of the droplets are below 10^{-6} cms. A number of experiments in which the mist was carefully collected and analysed and the water partial pressure measured, were carried out, and were in conformity with these conclusions.

For all of the curves shown in the figure, there is a definite point of intersection with the saturated vapour pressure line, but the angle of intersection and the height of the maximum decrease very rapidly with increase in initial hydrogen sulphate content. This maximum has no special significance beyond showing the amount of super-saturation which it is necessary to obtain in a gas before the particles can grow indefinitely. A pressure line corresponding to a supersaturation below the maximum (such as the line SS, Fig. 3) will cut a curve in two positions; only one of these, A, however, represents a stable system. This is the one corresponding to the smaller radius. A droplet whose conditions correspond to the point of intersection, B, would have the same vapour pressure as the surroundings, but, if an infinitesimal amount of water is added to, or subtracted from the droplet, it will immediately become unstable, and will either increase to infinity or decrease to the radius of the point, A. The point B represents a type of false equilibrium, and droplets at this point are in an unusual position in so far as the addition of water *reduces* their water vapour pressure and *vice versa*.

A number of interesting conclusions concerning the removal of sulphuric acid mist can be drawn from these results. Mist particles can be removed either by reducing their size so that their Brownian movement becomes very high, or increasing their size so that they settle out by gravity or can be thrown out by centrifugal force. Sufficiently small particles cannot be obtained merely by drying if the initial nucleus is greater than about 5×10^{-7} cms. radius, and below this size the vapour pressure of the medium does not make a very great difference to the Brownian movement of the droplets. It is more usual to remove sulphuric acid mist by settling or by centrifugal means.[29] A first requirement in obtaining large particles is to start with large hydrogen sulphate nuclei; the degree of supersaturation required being smaller, the larger the nucleus. Subject to the considerations given in a following paragraph, the particles can then grow to infinite size with a very small degree of supersaturation.

The curves explain the results of Remy,[15] who found that pure water

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[29] See paper by one of the authors (C. F. G.), this volume, p. 1218.

absorbed *sulphuric acid mist* much better than did concentrated sulphuric acid. A casual examination leads one to the reverse conclusion, as the intensity of a mist is always increased by passing through water, whereas it is decreased on passing through sulphuric acid. This is due, of course, to a very large change of particle size.

The absorption of mist by water has been demonstrated in the course of this research in a simple way. A long horizontal tube was half filled with water, and a stream of air containing sulphur trioxide passed in one end. The growth of mist particles along the tube was readily visible, and at low flow rates they fell to the water surface completely before reaching the end of the tube. With 30 per cent. sulphuric acid, on the other hand, no such growth or falling of the particles was observed.

These experiments illustrate the contrast between the absorbing media most suited for the removal of sulphur trioxide and sulphuric acid mist, respectively. For the former, extremely low water vapour pressure is essential, whereas for the latter saturated or supersaturated water vapour pressure is more effective. The overall efficiency of a washing tower will pass through a minimum as the absorbent liquid is changed continuously from 98 per cent. H_2SO_4 to pure water.

It remains to consider how long it will take for equilibrium to be established when the conditions of the carrier gas are changed. The rate of evaporation and condensation of water vapour from pure water has been determined experimentally by Alty and co-workers,[7] and it is probable that for sulphuric acid the rate will be the same when multiplied by the relative vapour pressures. Very approximate calculations from their results indicate that in one second after changing the conditions of the carrier gas, equilibrium within a few per cent. will be re-established. Probably the most serious cause of lag in the establishment of equilibrium will be the change of temperature of the droplets due to the condensation or evaporation of the vapour. A theoretical treatment of this has recently been made by Fuchs.[30] Townsend [8] showed that iodic acid mists could be rendered invisible merely by a passage through concentrated sulphuric acid, but that, on replacement of the water by subsequent bubbling through the latter, the original intensity of visible mist was obtained. Such experiments have been repeated with sulphuric acid mist in the present work, and it was found that strong drying agents, such as phosphorus pentoxide and concentrated sulphuric acid, readily reduced the size of the particles until they became invisible, and on passing over water the mist again grew to its original density. These experiments were carried out in a long tube and the rate of increase of the size of the particles could be easily seen. The experiments were purely qualitative, but sufficed to show that equilibrium was re-established in a few seconds.

Other Mists.

Any volatile anhydride which reacts extremely rapidly and practically irreversibly with water vapour, producing a non-volatile substance, will almost certainly be only partially absorbed when passed in an air stream through water. Acetic anhydride, chlorine heptoxide and nitrogen pentoxide are additional examples of substances which act in this way.

[30] N. Fuchs, *Physikal. Z. Sowjetunion*, 1934, **6**, 224.

In all these cases it is likely that the mechanism is the same as that described for sulphur trioxide in the first part of this paper.

It would also be instructive to draw vapour pressure-radius curves for mists arising from the anhydrides mentioned in the preceding paragraph. These curves would be similar to those in Fig. 3. As far as is known, the mists behave in the same way. Mists formed by the hydrogen halides with water (generally in the presence of foreign nuclei) belong to a more complex but especially interesting group. In these cases, both vapours are present in the gas phase. If the partial pressure of one of these vapours is taken as constant, curves representing the change in partial pressure of the other with radius could be plotted for droplets arising out of non-volatile nuclei of various sizes. These would be somewhat similar to those in Fig. 3. In the absence of nuclei, the curves would not fall below the equilibrium pressures for flat surfaces, and therefore no mist particles could be obtained except at high supersaturations. This is in agreement with the results of Aldis and Philip.[10] Askew [31] found that mist formed more readily with hydrogen bromide than with the chloride. This follows from the much lower partial vapour pressure of the bromide over its aqueous solutions.[32] It may be that the discrepancy between the calculated and observed sizes of hydrochloric acid mist droplets found by Jackson and Philip [11] would be removed if consideration were given to the above points.

Summary.

Recent measurements of the velocity of the reaction between sulphur trioxide and water vapours and the phenomena accompanying the production of sulphuric acid mist, are shown to support the explanation of Walker, Lewis and McAdams for the non-absorption of sulphur trioxide in water and its absorption in concentrated sulphuric acid. It is also shown that the size of the initial hydrogen sulphate nucleus is the important factor governing the change in droplet size with the change in the water vapour pressure of the medium. Curves have been drawn showing the growth of mist particles under various conditions, and their technical importance discussed. It is suggested that these considerations can be applied to other mists.

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        University College, London.

[31] H. O. Askew, *J.C.S.,* 1927, p. 966.
[32] Measured by S. J. Bates and H. D. Kirschmann, *J.A.C.S.,* 1919, **41,** 1991.

THE REMOVAL OF MIST BY CENTRIFUGAL METHODS.

By C. F. Goodeve.

The problem of removing droplets of oil or other liquids from air has been recognised as a difficult one. Very small drops (radius less than 10^{-6} cms.) with high Brownian motion are easily removed with filters, as they collide readily with the walls. Large drops (radius greater than 10^{-4} cms.) have a negligible Brownian motion, but may be taken out

easily by centrifugal separation. The removal of droplets of sizes in the intermediate range has not been completely accomplished, except by electrostatic precipitation methods. In this paper, centrifugal methods developed in the course of work on mists of various types are described.

Impinging Gas Stream Methods.

The method for the detection and removal of mist droplets, in which the air stream is caused to impinge as a fine jet against a clean glass plate, has been applied by many experimenters with considerable success. The
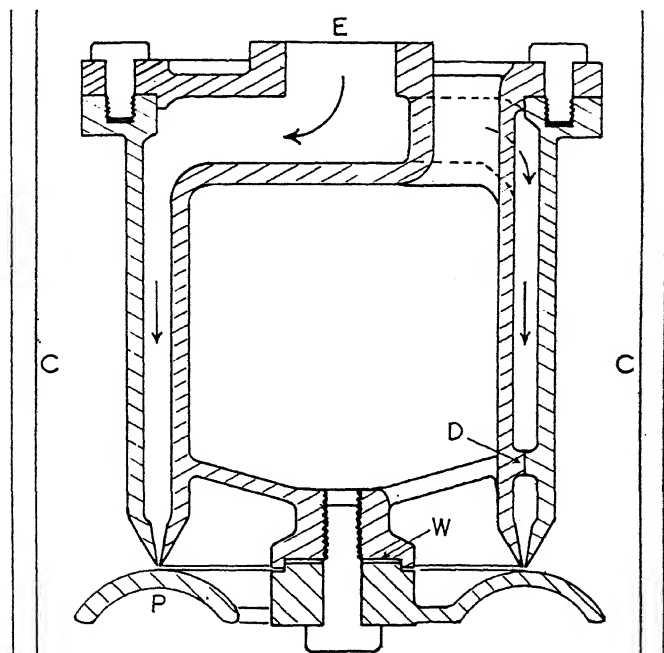
FIG. 1.—Cross-section of separator unit for the removal of mist droplets. E—Entry. D—Distance lugs. P—Collecting plate. W—Adjusting washers. C—Wall of container.

action depends on the centrifugal force on the particles during the rapid change in direction. This type of apparatus was modified by Calder and Fox [1] for use in the technical removal of sulphuric acid mist. In their original design, they used a large number of holes in plates arranged in series. They have improved their apparatus from time to time, and, in particular, they have found it more useful to apply a very high centrifugal force for a short period rather than a lesser force for a longer period.

The apparatus of Calder and Fox has the disadvantage that relatively wide jets have to be used to prevent stoppage and to give a reasonable capacity to the apparatus. These wide jets cause a reduced efficiency.

[1] Calder and Fox, *B.P.*, 1916, 126,320; 1922, 206,229; 1923, 228,646; 1924, 240,224.

In the apparatus described below, this difficulty has been avoided by using a narrow annular jet which allows a high capacity with a very short distance for the droplets to move transversely through the airstream. This apparatus has been used for some years on a technical scale to remove the mist droplets in the compressed air supplies (5 lbs. per sq. in.) of this laboratory and a number of others.

The final design of the apparatus, as prepared and made by Messrs. Reavell & Co., Ltd., Ipswich, is shown in the figure. The annular jet is $\frac{1}{64}$ in. wide and 12·4 ins. in circumference. Most of the pressure drop (generally 2 lbs. per sq. in.) takes place in the jet, producing a linear velocity of 370 ft. per sec. at the orifice. The air impinges against a collecting plate fitted close to the jet. The flow of the air is split into two parts, moving in opposite directions and at right-angles to the original flow, while the mist droplets carry on until they strike the collecting plate. The maximum thickness of air through which the droplets must pass is $\frac{1}{128}$ in. The air returns through the centre of the jet and along the outside, while the collected liquid falls through openings from the plate. The capacity of this separator unit for a 2 lb.-pressure drop is 30 cubic ft. free air per min. Generally two or three of these are used *in parallel* and are connected directly to the compressor.

Tests have been made on the content of oil droplets in the compressed air supply (arising from the high-speed rotary compressor) from time to time during the past three years. The separator units have been found to remove all oil droplets large enough to settle out and produce oil films in glassware and apparatuses commonly used with compressed air in the laboratory. Occasionally, however, it has been found possible to detect traces of oil by the jet and glass plate method referred to above. The units have not been found to remove completely the dust generally found in London's asmosphere. The efficiency may be increased by using a higher pressure drop and a smaller jet. The dimensions given, however, are convenient for general purposes.

The units have been examined every year and only a very small amount of grit has been found to collect in the annular jet. They have not been found so efficient for the removal of oil droplets in high-pressure air, owing, presumably, to the higher density of the medium through which the droplets must pass and to the greater turbulent motion produced at the jet. It may be possible to modify the design by the application of hydrodynamical principles to produce a device suitable for this purpose.

Filters.

The action of filters in removing mist droplets is mainly centrifugal [2]— droplets much smaller than the sizes of the pores being readily removed. A very simple and efficient filter has been formed from a layer of glass or silica powder on coarse sand. The finest grade of Jena sintered glass filters, No. 4, has an equally high efficiency and is very convenient to use. The pore size of this filter has been estimated by the makers [3] to be 2 to 5 × 10^{-4} cm

These filters have been tested with various mists. For example, sulphuric acid mist has been made under controlled conditions and tested before and after passing through the Jena filter, with a Tyndall beam from a Pointolite lamp. The size of the mist droplets was reduced continuously by lowering the partial pressure of the reactants until the blue mist just disappeared. It is estimated that the size of the droplets before the mist disappeared was 10^{-6} cms. In all cases no trace of a Tyndall beam could be seen in the air which had passed through the filter. Similar tests were made with hot exit flue gases from a power station boiler, with the same

[2] W. E. Gibbs, *Clouds and Smoke*, 1924, p. 88.
[3] See J. W. McBain and C. R. Dawson, *Proc. Roy. Soc.*, 1935, 148A, p. 32.

result.   Some filters have, however, been found to pass a certain amount of dust from the atmosphere, as detected by the single jet described above. Particularly is this the case when the filters were new and dry, but their efficiency always increased when used.

Although no evidence has been obtained to show the removal of droplets whose size is below that necessary to give a Tyndall beam, it is unlikely that such droplets pass through the filter.   Freundlich [4] has shown that, with a coarser filter, the optimum transmission occurs for droplets of 10^{-5} cms., and that droplets below this size are readily trapped by their Brownian motion.

These filters have often been used for determining the amount of sulphuric acid present in London's atmosphere in the presence and absence of fog.   A high velocity of flow was obtained by connecting the filter to the suction side of a vacuum pump, the discharge side being connected to a gas meter.   They have also been used to measure sulphuric acid mist in exit flue gases.   They have the important advantage of being inert to acids and they are readily cleaned.   They may find uses in other problems connected with the analysis of mists.

It is important to recognise that filters do not give the concentration of the mist droplets but only the total content of the non-volatile components.

(*Added in Proof.*)

Removal of Fogs and Smoke by Falling Drops.

The interesting problem of the removal of smoke or fog particles by falling raindrops has been referred to by Dr. Dobson.   A particle in the path of a falling drop will be caught, providing its inertia is sufficient to overcome the outward flow of air in front of the drop,   It can readily be seen that the chance of a particle being so caught will be unity if it lies on the axis of the path, but will fall rapidly as its distance from the axis increases.   The chance will also increase as the velocity of the falling drop is increased.   The relation in this case is, however, rather complicated. Heavier particles will, of course, be trapped more easily than lighter ones.

A few experiments were made with an apparatus in which a drop of a definite size could be maintained on the end of a very fine capillary tube in an upward flowing air stream containing sulphuric acid mist.   It was found possible to vary the size of the drop and the velocity of the air stream over quite wide limits.   Measurable quantities of sulphuric acid were found in the drop after a short run but the effects of the variables referred to above were not studied.

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London.

[4] H. Freundlich, *Colloid and Capillary Chemistry*, 1926, p. 785.

GENERAL DISCUSSION.*

Dr. B. W. Bradford (*Billingham*) said :   The curves given by the authors (Fig. 3) for the growth of sulphuric acid droplets refer rigidly only to aerosols at infinite dilution.   In practice, aerosols of the concentrations usually encountered in any but meteorological work aggregate so rapidly that vapour-pressure equilibrium cannot be attained except in the final stages of growth, when the particle concentration has diminished to very low magnitudes.

* On the two preceding papers.

Particle size determinations by several methods on a highly concentrated sulphuric acid mist (15 g./M^3) produced by hydration of SO_3 in the presence of excess water vapour, gave concordant results, which agreed well with the rate of aggregation calculated from the Einstein-Smoluchowski formula. A particular search was made for inhomogeneities of droplet radius : it was found, however, that the variations were less than the experimental error of about 5 per cent.

In the practical determination of mist concentrations in saturated gases by methods involving a sudden pressure drop (e.g. filtration or impingement) it is important to note that the apparent mist concentration may be appreciably increased by condensation of vapour due to cooling by expansion at the orifice. This source of error is usually greater than that due to the fact that vapour pressure equilibrium in the aerosol refers to a highly curved surface while in the mist-sampling apparatus the surface on which the scrubbed mist collects is approximately plane.

Professor H. Köhler (*Uppsala*) said : How does Dr. Goodeve explain the condensation in a Wilson chamber, where the supersaturation is so great. Again, does the Aitken Nucleus Counter really give the number of nuclei ; it is generally believed that the number of droplets formed, is the same as the number of nuclei.

Mr. C. F. Goodeve (*London*) (*communicated*) : Clusters will be stabilised if given an electric charge, owing to the increased attraction to the polar water vapour molecules. Nuclei will, in general, facilitate condensation and, if present in sufficient numbers, prevent the attainment of the degree of supersaturation necessary for the growth of clusters to droplets. Under most conditions, therefore, the Aitken Nucleus Counter will probably give the correct result.

Dr. N. Fuchs (*Moscow*) (*communicated*) : To the three stages of formation of a sulphuric acid mist mentioned by Dooley and Goodeve, one more must be necessarily added, namely the coagulation of the growing nuclei and of the finally developed droplets. The rôle played by coagulation in the formation of the sulphuric acid mist can be seen, e.g., from our experiments in which, by a quick mixing of two air-jets containing vapours of water and sulphur trioxide at partial pressures of about 1 mm., a primary mist was formed containing about 10^{11} droplets per c.c. of $1 \cdot 2$ to $1 \cdot 5 \times 10^{-6}$ cm. radius. Such a mist coagulates with a tremenduous velocity, and in one second the number of particles per c.c. is reduced about a hundredfold, and the mass of the droplets accordingly increased.

Mr. A. Dooley (*Birmingham*) (*communicated*) : It is incorrect to say that the Calder-Fox Scrubber is limited to " wide jets used to prevent stoppage and to give a reasonable capacity to the apparatus." In a modified form, now in general use, the scrubber is built up of glass strips arranged to give narrow slits behind which are supported further strips on edge. This design permits the adoption of the most suitable dimensions and clearances for any particular purpose. Units with 1/32-inch slits are in use on, for example, sulphuric acid concentrators but, if necessary, 1/64-inch slits could be arranged by using ground glass strips.

Blocking of the slits by solid matter depends on slit dimensions, and on the position and arrangement of the striking or " back " plate. In the Calder-Fox apparatus referred to above, overlap of the " back " strips is a minimum. No advantage in this direction could be claimed for Mr. Goodeve's apparatus.

While admiring the design of Goodeve's apparatus in so far as it is applied to the particular purpose stated, viz., the removal of oil mist from 30 cubic feet of air per minute, I feel it necessary to point out that there would be serious limitations to its application to systems on which the Calder-Fox Scrubber is employed. On a technical scale gas volumes of upwards of 1000 cubic feet per minute are frequently handled, and it is evident that a circular form of apparatus would be unwieldly if in one unit or, if the necessary capacity were obtained by multiplication of

smaller units, unnecessarily complex. Furthermore, the question of materials of construction would require consideration if corrosive fumes were to be handled, and here also the Calder-Fox Scrubber appears to have the advantage.

Dr. N. Fuchs (*Moscow*) (*communicated*) : The chief rôle in the removal of the droplets of 10^{-5} cm. radius and less by means of porous and fibrous filters is played, not by the centrifugal forces, but by the Brownian movement of the droplets. This may be seen, *e.g.*, from the fact that such droplets pass the filter more easily the larger the linear velocity of flow through the filter. Centrifugal forces would evidently give the opposite relationship. The same conclusion may be reached theoretically by calculating the effect due to inertial forces by the method of Albrecht.[1]

It is difficult to estimate correctly the efficiency of the glass filters spoken of by Goodeve in respect to sulphuric acid mists, because he does not indicate the velocity of flow in his experiments. It is doubtful whether the finest mists in these experiments consisted of droplets as large as 10^{-5} cm. As was shown in our laboratory,[2] no Tyndall beam can yet be observed in highly concentrated (10^9 droplets per c.c.) sulphuric acid mists with droplets of even 3×10^{-6} cm. diameter (arc lamp illumination.)

Mr. C. F. Goodeve (*London*), said :

In reply to Dr. Bradford and Dr. Fuchs : The vapour of a droplet formed as a result of a collision between two droplets remains practically unchanged except when the droplets are below visible dimensions. This can be confirmed by a careful examination of Figs. 2 and 3. It is, of course, impossible to represent, in a single diagram, all variables which occur in practice.

In reply to Dr. Bradford : I have emphasised in my paper on centrifugal methods that it is impossible to determine a mist concentration (expressed either as number of droplets or grams, per unit volume) by any apparatus in which the droplets are removed. This arises from the fact that removal invariably alters the surface area and curvature. Centrifugal methods can only be used to determine the concentration of a non-volatile constituent of a mist and, of course, condensation of vapour due to cooling does not in any way enter.

In reply to Mr. Dooley : I agree that the modified form involving the use of glass strips is a considerable improvement over the previous type of apparatus. Unless wedge-shaped glass strips are used, however, there will be a very large loss of power in obtaining the linear high-speed flow desired for efficient removal.

[1] Albrecht, *Physikal. Z.*, 1931, **32**, 48.
[2] Fuchs and Oshman, *Acta Physicochimica U.R.S.S.*, 1935, **3** 61,

PART II. : THE INDUSTRIAL ASPECTS OF DISPERSE SYSTEMS IN AIR AND GASES. INTRODUCTORY PAPER.

By R. Lessing.

Disperse systems in gases in their relation to the problems of industry and the amenities of life have not yet received the close study which their ubiquity and practical importance demand. The present survey is therefore not intended to be a record of work done, but to indicate the problems which still await solution and the directions in which the results

of fundamental investigations can and should be applied in practice. The dispersoids to be considered comprise solids, liquids, solids covered with liquid films and liquid droplets containing solid nuclei.

Some of these systems happen to occur in many industrial operations, some form natural phenomena of climatic conditions, others are undesired concomitants of the atmosphere peculiar to civilised conditions of life and work, whilst yet others such as war gases and smoke screens, are set up intentionally as products of the latest developments of human activity.

Dust.

The most common and quantitatively most important solid dispersoids are dusts. Systems containing these are probably also the simplest, and may therefore be considered first.

The most prolific source of dust production by man is grinding for size reduction, and this operation is carried out in the manufacture of flour, cement, fertilisers, coal, lime, chalk, gypsum, pigments, dyes, glass and pottery materials, rubber fillers, fish meal, potato meal and others. The total production of these materials in powder form approaches 20,000,000 tons per annum in this country.

All these industries comprise processes in which at some stage dust is dispersed in air. For reasons of economy, health and comfort, it is necessary to recover this dust and purify the air ; hence, apparatus for dust collection is an essential component of their equipment.

Other types of dust, produced by abrasion, occur in the surface grinding, polishing and sandblasting industries. The quantities involved are of a much smaller order, but collection is not less difficult on account of the multiplicity of point sources of dust emission and their proximity to the respiratory organs of the workers.

Into this category falls the dust formation by drilling shot holes in mining and quarrying operations. In coal mining and handling, dust is raised in large quantities and high concentrations during blasting, loading and unloading, and particularly in screening. Some of this is formed by the disruptive action of explosives on the shale or sandstone and on the massive coal, and some is due to the dispersion of the more friable components of the coal seams. An intentional application of dust takes the form of " stone dusting " of underground roadways and working places for the prevention of coal dust explosions. There is at least one form of dust, *viz.*, road dust, that is rapidly diminishing, and has already disappeared from our principal highways, which are no longer constructed with waterbound, macadamised surfaces liable to severe attrition.

A problem affecting every individual is that of domestic dust and its collection after settlement by sweeping or by modern suction methods.

Smoke.

True smokes, defined as dispersions in gases of solids formed by condensation and aggregation or coagulation occur in practice mainly in metallurgical operations in which metals or metallic oxides are volatilized by heat, either in bulk as in the " distillation " of zinc, or as the result of unavoidable side-reactions, as in most smelting operations. The recovery of valuable metals dispersed in waste gases as smokes is an important adjunct of modern metallurgy.

Common domestic " smoke " cannot strictly be grouped among the true smokes for reasons discussed below ; the only true type of carbon smoke is the system formed by complete thermal decomposition of hydrocarbons or other volatile carbon compounds in which no liquid products are left.

Fog.

Fogs are usually regarded as dispersions of liquids in gases, but it is questionable whether pure liquids are capable of fog formation without the aid of heterogeneous nuclei. Neither in meteorology nor in industry can systems be contemplated which are free from solid particles or substances soluble in the liquid dispersoid. Any definition of fogs as the formation by condensation of liquid droplets in the gas phase, must therefore comprise the presence or formation of dust or smoke particles, or of compounds soluble in the liquid phase. In practice, matters are complicated by the presence of a number of different kinds of particles or compounds, some of which are frequently unidentified and of unknown structure, composition and effect. The meteorological aspects of fog formation do not come within the scope of this paper, except as far as the supply of solid nuclei and of sulphur oxides from flue gas emission is concerned. The bulk of the chloride nuclei are, of course, derived from sea-water spray, but some hydrogen chloride is due to chloride in coal released upon its combustion.

An industrial fog of considerable technical importance is the tar fog in crude coal gas and coke oven gas. The tar droplets formed in the gas leaving the carbonising retorts or ovens by the rapid drop in temperature, give it the typical reddish-brown colour. I am not aware of any precise work on the structure of the droplets, their size distribution, and rate of coalescence, but there cannot be any doubt that the " free carbon " particles formed by the thermal decomposition of the primary decomposition products of coal, are the nuclei on which the liquid tar, together with water, or rather a solution of ammonium salts, condenses. The " free carbon " still contains several groups of asphaltic or bituminous substances.

The dispersoids of tar fog are therefore themselves a multiphase system ; the principal phase is a complex mixture of hydrocarbons, oxygenated bodies, bases and pitch, and has a wide boiling range. They are dispersed in a gas phase containing, *inter alia,* the lower boiling hydrocarbons, which are solvents for the condensate. This system, which rapidly passes through a temperature gradient from 900° C. to 15° C., offers an interesting field of investigation. The persistence of some residual tar fog through the condensing system and the following gas purifying train, has recently led to the installation of electrical tar precipitators for the almost quantitative extraction of tar in fog form.

The formation of " gum " in coal gas is a phenomenon which has only recently become apparent since the adoption of the practice of eliminating naphthalene and some of the benzene hydrocarbons from the gas. The cause of " gumming " is not yet fully explained, but it is probably due to the action of nitrogen oxides on certain gas constituents ; the reaction products are peculiar in coalescing from the dispersed state to tough masses when the gas passes through narrow orifices or channels.

In the manufacture of sulphuric acid, and particularly of oleum, the waste gases carry droplets of the acid in fog form. Presumably there are sufficient fine dust particles present, some of which are lifted from the

catalyst or catalyst carrier, which act as nuclei for the drop formation. This industry and the sulphide roasting industry were among the first to employ electrical precipitation for breaking up these very persistent acid fogs.

Oil fogs occur widely; the most common form is that of the exhaust from motor engines, where solid nuclei are always provided by the " carbon " formed on incomplete combustion of the petrol air mixture. The oil fog from the lubricants of gas compressors is probably formed by a different mechanism. Decomposition at high temperatures does not take place and the cause must be sought in the stripping of the oil film on the cylinders at critical gas velocities.

The persistant fogs resulting from fatty acid distillation, rosin distillation or gum running must be classed as smokes, inasmuch as the dispersoids in the cooled system are more or less solid.

The Flue Gas Problem.

The burning of fuels results in the creation of disperse systems in gases whose practical importance is only equalled by their theoretical interest and technical complexity. Even in the case of the combustion of gases—complicated enough *per se*, but relatively simple in comparison with that of solid fuels—disperse systems may be set up in the absence of a suitable excess of, or inadequate mixing with air, resulting in a smoky flame.

Liquid fuels in drop form are dispersed in air by spraying into the combustion chambers of furnaces or into the cylinders of internal combustion engines. The velocity and completeness of combustion depend, apart from the chemical and physical characteristics of the fuel itself, upon the subdivision and disposition of the liquid in the gaseous phase. The mechanism of " knock " during combustion under high compression has been studied intensively during recent years and the various theories advanced for it depend on the correct interpretation of the structure and behaviour of the disperse systems involved.

The combustion of coal provides a vast field for the study of disperse systems in gases. Quantitatively, its importance may be gauged from the fact that the portion of coal emitted from industrial and domestic chimneys constitutes the great bulk of the polluting matter dispersed in the atmosphere of civilised countries. For a thorough understanding of the kind and amount of this emission it is necessary to consider the chemical and physical characteristics of the fuel itself, its behaviour during the combustion process and the products resulting from it.

Coal is in every respect a most heterogeneous material, as is obvious from the great variety of vegetable matter which has formed the raw material, the manner of its deposition and the different biological, chemical and geophysical agencies which combined to transform this material into coal as we find it. The different kinds of coal characterised by containing four distinct rock types (vitrain, clarain, durain, fusain) in different stages of " coalification " (rank) determine the behaviour of the fuel during the combustion processes. With each of these are associated inorganic substances of characteristic composition and in characteristic proportions, together with adventitious mineral impurities derived from the strata below, above and between the coal seams.

The mechanism of combustion in a fuel bed is complicated by the fact that combination with the oxygen in the air can only take place on the

surface of a piece of coal. The rise in temperature causes layers below the surface to be subjected to thermal decomposition (carbonisation) by which combustible gas and tar are liberated. Under the aerodynamic conditions controlling the burning mechanism, some of this volatile matter escapes so rapidly from the high temperature zone that its combustion is not completed. Unless it is subjected to contact with hot surfaces such as a furnace arch, and possibly to the action of secondary air, a portion will escape in form of tar suspended in the flue gases. Some may be heated high enough to suffer secondary thermal decomposition, but only after a time lag long enough to permit its escape from the combustion zone. In this case " soot " is formed. Firing conditions permitting the escape of tar vapour or soot do not obtain in modern, well-conducted furnace operations. They are, however, the concomitant of the customary management —or lack of it—of the open fire in the domestic hearth. The tar content of deposits from the atmosphere of towns can therefore be traced back with certainty to this source and its amount forms a measure of the chimney emission from domestic fireplaces in which raw coal is burned.

The portion of the organic coal substance which is emitted from industrial furnaces or any fires operated with air and flue gas currents of high velocity, is in form of coke particles or partially burned coal particles. The former are frequently cenospheres formed by the swelling and blowing into bubbles of individual coal particles during a carbonising stage which was arrested when the empty shell was completely coked and had assumed rigidity, the hollow particle escaping from the furnace and combustion by reason of its balloon-like structure and low volume-weight. Coke cenospheres are formed in great number in pulverised fuel fired furnaces, where the sub-division of the raw coal into fine dust particles favours the occurrence of this phenomenon.

Relative to its proportion in the coal fired, the ash contributes a much greater quota of polluting matter than the combustible coal substance. The reasons for this are closely bound up with the character of the various mineral substances in the coal components and their behaviour during combustion.

The position is fairly simple in the case of buring coal in powder form. Here small coal particles, irrespective of the components they represent, are individually subjected to combustion dispersed in about 13,000 times their own volume of air, so that they are rapidly and fairly completely burned. Each particle of coal leaves its ash, again in particulate form, suspended in the flue gas. Owing to differences in their composition, these ash particles behave in different manner. Those of low fusion point are at the furnace temperature in form of liquid drops. Some of these drops, mostly in form of hollow spheres or ovoids, pass forward and retain these shapes when cooled. Many collide with each other and coalesce—as in other liquid-gas systems—or attach themselves to more refractory and still solid particles. When such aggregates become too heavy they are deposited at points determined by the velocity and the viscosity of the gases. Such sedimentation may cause the formation of masses of clinker (bird's nests). I have shown [1] that the size and basicity of ash particles or aggregates in a coal dust firing system diminishes from the combustion chamber towards the chimney, and that the solids emitted from the chimney may consist of highly silicious and refractory single particles.

[1] Lessing, *Trans. Second World Power Conference*, Berlin, 1930 ; *Fuel in Science and Practice*, 1930, **9,** 348.

Pulverised fuel furnaces send forward about 70 per cent. of the ash in the coal fired, and dust extraction plants are therefore incorporated in most modern installations.

Coal fired in pulverised form accounts only for about 4,500,000 tons or 2·8 per cent. of this country's total consumption. The great bulk is fired in the size ranges obtained from the collieries, i.e., pieces from 12 inches down to the dust particles naturally contained in coal. Some 90 per cent. of the ash remains behind, but the balance derived from coal particles detached by decrepitation or from minerals finely disseminated through the mass, is small enough in particle size to be carried by the current of combustion gases before coalescence with larger pieces can take place, and unless deposited in the flues, is emitted from the chimney.

It is worthy of note that the natural dust in coal, in which the charcoal-like fusain is concentrated, is particularly liable to be raised by the gas currents, owing to its non-coking character and consequent failure to fuse and coalesce during the carbonising stage. Much of this is therefore carried out of the fuel bed before the combustion is completed. Coal as mined contains about 4 per cent. of dust smaller than $350\,\mu$. The British consumption of 161,500,000 tons (1934) per annum included, therefore, 6,400,000 tons of this potential contribution to atmospheric pollution.

It is interesting to compare this with the total amount of solid matter found in the atmosphere, and the case of London may serve as an example. The coal consumed in Greater London in 1934 was 19,282,000 tons. Its mean dust content at 4 per cent. amounted to 771,280 tons, with an ash content of, say, 15 per cent. It may be fairly assumed that from this coal dust all its 15 per cent. ash and 7·5 per cent. of carbonaceous matter which has escaped combustion, are discharged into the atmosphere. This means a total of 173,500 tons of flue dust derived from coal dust and emitted over the 700 square miles of the London area. According to the 21st Report of the Atmospheric Pollution Committee the total deposit over these 700 square miles during the corresponding period (taking the mean of the amounts collected in all deposit gauges as representative for this area) was 184,000 tons. The portion of this total consisting of carbonaceous matter and insoluble ash plus one-half of the soluble ash (sulphates) amounts to 124,500 tons, and may be compared with the emission derived from the natural dust in coal. Whilst the pollution caused by coal dust appears to be actually greater, it must be remembered that perhaps only 15 per cent. of the solids suspended in the atmosphere settle or are washed out by rain and are caught in the gauges. Allowing for this, it appears that the natural dust in coal may be responsible for 20 per cent. of the pollution of the atmosphere with solids. As means for separating this dust are available, its elimination and utilisation under conditions permitting the collection of its ash would greatly assist in the abatement of the pollution of the atmosphere with solids.

The sulphur in coal, present partly in inorganic form in pyrites and partly in organic combination, is almost completely liberated during combustion. The greater portion escapes as SO_2, and a small portion as SO_3. I have given an estimate of the minimum annual sulphur emission over London [2] of 500,000 tons, expressed as sulphuric acid. Much of this remains in gas form, and a large part is retained by way of corrosion of metals, disintegration of building materials and action on textiles and

[2] Nat. Smoke Abatement Soc., Proc. 7th Annual Conf., Bristol, 1935.

other organic matter.   From the point of view of disperse systems in gases, two forms must be considered ; sulphuric acid nuclei present in town air, especially during fogs, and sulphate particles formed by the neutralisation of basic dust, notably lime, and oxidation during a stage of favourable p_H condition.

The presence of oxides of nitrogen (NO and NO_2) as normal constituents of combustion gas has not received much attention in the past, but is now becoming important in connection with flue gas washing processes.   Their concentration in industrial flue gases is of the order of 0·1 to 0·2 mg. per litre in terms of nitrogen, but may vary with the combustion conditions.   Apart from their probable effect on the oxidation of SO_2, they are of interest in view of Coste and Wright's [3] work on the formation of nitrous acid nuclei.

Chlorine, which is present in many coals in amounts up to 0·5 per cent., appears in the products of combustion mainly as alkali or iron chloride, or as hydrochloric acid, and thus adds a little to the chloride content of the atmosphere derived from sea-water.

The form in which fluorine, the presence of which in some coals has been established,[4] is liberated on combustion is not yet known.   In carbonisation it is present in the gas as hydrogen or ammonium fluoride. Though small in amount, this element will have to be regarded in future as a potential contributor to atmospheric pollution.

In the carbonising process accompanying or preceding combustion as in the domestic fire, indicated by liberation of tarry matter, ammonia is emitted which combines with SO_3 or SO_2 and causes the formation of water soluble nuclei.   These (where dispersed in air) behave similarly to the nuclei of NaCl derived from sea-water spray.

Dust in Mining.

Coal causes dispersion of solids in the air even before it is burned. In mining, dust is released and is carried by the currents of ventilating air and precipitated from them in the workings.   The risk of its inflammation and of underground explosions caused by it is an important subject of investigation by those concerned with the safety in mines. The physical and chemical mechanism of the use of stone dust to prevent explosions requires still to be fully explained.

In the preparation of coal on the surface, the effective collection of dust from the air, notably in screening operations, is as yet an unsolved problem.

The silicious rocks associated with coal are responsible in some districts for a considerable number of cases of silicosis.   The problem of the prevention of this terrible disease calls for the close study of suspension in air of particles of quartz, shale, sericite and other minerals, of sizes below $5\,\mu$ formed by drilling, shot firing and other underground work. In some operations as in drilling, dispersions of the coarser dust may be avoided by suitable filters.   For the fine dust raised by shot-firing, spraying with water and wetting agents is being experimented upon. Fundamental work has only recently been undertaken, and it is hoped that the results of this symposium will be of use in the practical solution of this problem.

[3] Coste and Wright, *Phil. Mag.*, 1935, 7, **20**, 209.
[4] Lessing, *Nature*, 1934, **134**, 699; *Fuel in Science and Practice*, 1934, **13**, 347.

A better knowledge of the principles of dispersion of solids in gas will also assist on the clinical side of silicosis, for the passage of the silicious matter through the respiratory system and its retention by the lungs involve phenomena not unlike those underlying the operation of industrial filters or scrubbers.

Methods of Cleaning Gases.

Industrial and meteorological disperse systems of solids or liquids in gases are, without exception, undesirable. The practical problems involved deal, therefore, with their breaking-up and the removal of the dispersoids from the gas phase. The methods principally employed are sedimentation in large chambers, centrifugal separation, filtration, electrical precipitation and washing with liquids in spray or film scrubbers.

Sedimentation involves the slowing down of the currents of gas carrying dust by expansion in chambers large enough in cross-section to permit the particles to settle out by gravity. Within the limits of space available in practice only the coarser particles settle effectively, although they may carry down some of the finer with which they collide in their downward path. In some cases baffles are provided to arrest particles by impact and turbulence is reduced by sub-dividing the current by means of vanes.

A common form of mechanical dust separator is the " cyclone," a cylindrical vessel into which the gas is introduced tangentially. The dust particles or droplets of liquid are thrown out by centrifugal force, arrested by friction on the wall of the cylinder and drop into the conical collecting base, whilst the gas leaves by a central tube. The efficiency for removing dust larger than $20\,\mu$ may be fairly high if the apparatus is designed to keep particles once thrown to the periphery out of the turbulent zone near the vertical axis of the apparatus. Many special contrivances have been proposed to achieve this object, but the extraction of particles below $20\,\mu$ requires a more intensive study of the size range and shape of each kind of dust, the temperature and viscosity of the carrying gas and a thorough exploration of the zones of streamline and turbulent flow in the vessel at varying gas velocities and pressure drops.

Filtration through fabrics or other porous layers provides a positive means of dust removal from gases. The disadvantage is the high resistance and its rise caused by the increase in the thickness of dust layers on the surface of the textile or other filter. Mechanical devices for shaking filter bags intermittently are usually employed. The permeability for fine particles varies with the original texture of the fabric, its age and condition and the thickness of the layer covering it. The need for subdivision into small units to avoid excessive resistance, makes the system very cumbersome where large volumes of gases are concerned.

In the thirty years since Sir Oliver Lodge's early experiments were applied in practice by Cottrell, electrical precipitation has been put to industrial use on an extensive scale. In broad outline the system is extremely simple. The gas to be purified is ionised by the corona discharge from negative electrodes of small radius of curvature (wires, thin rods, chains, grids) ; on their way to the positive, collecting electrode of large radius of curvature (tubes or plates) some of the ions attach themselves to the dispersoids, charge them and cause them to travel in the same direction. The electric current employed is of the order of 0·10 to 1·0 amps. at a pressure between 20 and 75 kv., the collecting electrode

being usually earthed. The technical development has been mainly concerned with means for producing, conducting and insulating against, the high-tension current required; with the form of the electrodes, the dimensioning of the gas passages and the design of rapping or other devices for removing dust from the positive electrode. In some cases the discharge electrode also collects some dust carried there by a minority of positively charged ions.

Much of the work done has been of an empirical kind, and was directed to the special needs of various branches of industry and the particular nature of the dusts, fogs or mists to be treated. The removal of liquids, say sulphuric acid or tar, from the collecting surfaces is easy, but dusts differ greatly in adhesiveness and conductivity and some may, by building up on the surfaces of the electrodes, affect the electrical conditions appreciably, so that non-conducting dusts may require moistening or the addition of conducting dust to the gas as well as mechanical vibration or scraping to keep the deposited layers of reasonable thickness and permeable to discharge.

The electrical precipitation industry has arrived at a stage of development where information on the properties of dispersoids, such as size, size distribution, shape, density, composition of particles, their surface properties and electrical conductivity, and the critical examination of the results will be of great assistance in its further development.

Washing of gases with water is probably the most effective method for the elimination of dispersoids in them. In gas works the scrubber packed with coke or wooden grids has served from the beginning of the industry for the extraction of ammonia and incidentally removes tar nuclei. Its modern equivalents are the rotary scrubber and towers filled with contact rings.

In air conditioning plants the control of humidity by water spraying devices is accompanied by the extraction of suspended solid particles. These plants usually incorporate eliminator baffles on which the unvaporised excess of water in drop form is arrested.

The treatment of flue gases by wet methods has assumed considerable importance during the last few years. After the claims of the aggrieved owner of land damaged by sulphur gases from the Barton Electricity Works of the Manchester Corporation were sustained by a judgment of the House of Lords in 1929, the Electricity Commissioners insisted that at the new London power stations to be erected at Battersea and Fulham, the necessary steps should be taken to eliminate practically all the sulphur oxides from the combustion gases of their boilers before discharge to the atmosphere. The magnitude of the problem will be realised if it is considered that each of these power stations when completed and working under full load will discharge nearly 2,000,000 cubic feet of flue gases per minute, and that before washing they contain 1 grain of sulphur per cubic foot (2·3 mg. per litre) and 1·25 grains dust per cubic foot (2·8 mg. per litre).

In the preliminary work it was soon found that any method capable of extracting nearly all the sulphur will, *ipso facto*, remove the dust to at least the same degree, since dust is removed from the gas phase immediately it is wetted, whilst the absorption by water of SO_2 and its oxidation to SO_3 if desired, require a measurable time of contact.

The methods employed at Battersea and Fulham differ in several important respects. At Battersea [5] a spray system is employed common

[5] Hewson, Pearce, Pollitt and Rees, *Proc. Chem. Eng. Group*, 1933, **15**, 67.

to all the boilers, the washing water is allowed to become acid in the first stage during which iron is added for the catalytic oxidation of SO_2 to SO_3, and the effluent after neutralisation with chalk and clarification is discharged into the Thames. At Fulham an individual washer of the grid type is provided for each boiler, a lime or chalk suspension is continuously circulated in film form over the grids and only a small purge corresponding to the sulphur and dust extracted is withdrawn, clarified and returned into the cycle. The mud containing calcium sulphite, calcium sulphate and dust is discarded, but no effluent is sent into the river. In an auxiliary scrubber through which air is passed, the sulphite in the circulating liquor can be completely oxidised to sulphate, if required.

In the experimental work carried out in connection with the Fulham plant, I found that the principal difficulty did not lie in achieving the high sulphur extracting efficiency stipulated, but in preventing the incrustations of calcium sulphate deposited on the scrubbing elements. These were traced to excessive supersaturation taking place in the liquor as a result of the repeated absorption of SO_2 and the oxidation of the calcium sulphite formed. Methods for de-supersaturation were evolved, which are incorporated in the Howden—I.C.I. system [6] installed at Fulham and already in operation at the Tir John Power Station, Swansea.

In view of the immense fuel consumption of modern power stations, and the replacement by them of a multitude of uncontrollable point sources of pollution, the technical possibility of complete purification of their flue gas emission will prove to be an important step in the reduction of undesirable dispersoids in our atmosphere.

50 *Queen Anne's Gate,*
   Westminster, S.W. 1.

[6] Pearson, Nonhebel and Ulander, *J. Inst. Fuel,* 1935, 8, 119.

GENERAL DISCUSSION.

Dr. R. Lessing, in introducing his paper, pleaded for precise definitions of the various types of dispersoids in gases. He considered that the outcome of this General Discussion would be of great value even if it only resulted in the acceptance of a reasoned nomenclature in the light of the papers submitted, quite apart from the subject-matter of the work itself.

Mr. A. G. Grant (*Darlington*) said : This paper covers a field too vast to be discussed adequately in so short a time, but our thanks are due to the author for his able review of industrial dispersions ; the subject matter of the paper is, in fact, the *raison d'être* of the meetings. Apart from the more academic interest of dispersoid investigation, its main object is to evolve such an understanding of the nature and properties of suspended matter in gases as will allow of their effective avoidance or removal on the industrial scale. In few cases is it necessary artificially to produce a gaseous dispersion, whereas removal is an almost universal problem. I hope that some of us may be able to abstract and summarise the papers we have heard in the light of their industrial applications.

I would like to support Dr. Lessing in his plea for a standardised nomenclature. We have a plethora of rather vague terms—dust, mist, fog, haze, fume, and the like—and none has yet found a concise and accepted definition.

One regrets that no detailed work is reported on the formation and nature of tar fog, a dispersion of very great importance in the fuel industries,

and hopes that Dr. Lessing's reference will stimulate further basic investigation.

The occurrence of so-called gums in town's gas is an interesting case of an extreme dispersion in that the gum concentration is of the order of 10^{-6} grammes per cubic meter.

We require much more accurate knowledge regarding the electrical precipitation process. Investigation would fall broadly into two spheres :

(a) The " pure electric " phenomena centring round the corona discharge in various gases and with various field shapes.

(b) The dispersoid phenomena, which can be sub-divided thus :—

(1) The charging of dispersoid particles and the mode of their removal from the gaseous medium.

(2) The phenomena and their control arising from deposition of the dispersoid on the electrodes.

These problems are fundamental to the design and understanding of electrical precipitation plant. Whilst various contributions have been made towards their elucidation, the electrical precipitation process remains as one designed and operated largely on an empirical basis. Where mathematical relations are known, these are used for comparative and co-ordinating work rather than for basic design.

Mr. W. A. Damon (*London*) said : I am particularly interested in that part of Lessing's paper which deals with the contamination of the atmosphere by the carbonaceous dust loosely adhering to coal. If burned in the ordinary way, much of it will certainly be emitted to atmosphere, together with the flue gas and, if as is done in some places, it is dumped on the spoil bank, it will be very likely to initiate spontaneous combustion. Many of the burning pit banks which are so prevalent in the North of England are due to the indiscriminate dumping of excessive carbonaceous matter. Therefore, I am much in sympathy with his plea for combustion under conditions which allow of the collection of the ash.

Lessing says that of the mass of solid matter suspended in the air over any area about 15 per cent. will be deposited. How did he arrive at this figure, and what happens to the remaining 85 per cent. Presumably when a South wind blows, towns to the North of London suffer more from London's pollution than from their own.

Mr. C. H. Bosanquet (*Billingham*) said : Dr. Pearson and myself are partly responsible for Dr. Lessing's figure of 15 per cent. for the fraction of the total emitted particles caught in deposit gauges in London. He arrived, I believe, at the figure by comparison of the deposit gauge figures with the estimated total emission, and asked our opinion on the subject.

The equations developed in our paper lead to the expectation that in fine weather only about 10-20 per cent. of the particles of diameter 20μ will be deposited in London, and an infinitesimal fraction of particles of the order 1μ. The remainder will drift across Europe, becoming more dilute as the cloud diffuses upwards and sideways.

The fraction 15 per cent. probably represents the fraction of the time that it is raining, when nearly all particles will be brought down near their point of origin.

Dr. R. Lessing (*London*), in reply, said that the figure of 15 per cent. as the proportion of the total solid matter in London air settled or washed out by rain (as determined by the deposit gauges of the Atmospheric Pollution Committee) was an estimate at which he arrived taking all known factors into account. This was confirmed by Mr. Bosanquet on a mathematical consideration of the sedimentation of particles at average wind velocities.

TWENTY-FIVE YEARS' PROGRESS IN SMOKE ABATEMENT.

BY J. S. OWENS.

The selection of a title for this paper was prompted by the fact that it was in 1912 the organised investigation into the degree of atmospheric pollution by smoke commenced. The starting-point of the investigation was very definite: At a conference held at an International Smoke Abatement Exhibition in London, the following resolution was moved by the author:—

" That in the view of this Conference it is desirable that immediate steps should be taken to decide upon and secure the general adoption of a standard method for the measurement of atmospheric pollution by smoke and other products of combustion and heat, in order that the data now being collected may possess a comparative value, and that a Committee be appointed to draw up details of a standard soot and dust-measuring apparatus and methods of its use."

The original Committee continued its work on a voluntary basis for several years. A number of Municipal Authorities had by then associated themselves with the investigation, and a grant in aid of the expenses was obtained through the D.S.I.R. The Committee then functioned as an " Advisory Committee on Atmospheric Pollution " in association with the Meteorological Office and was subsequently attached to the Air Ministry. The work continued to expand and the control of the investigation ultimately passed to the D.S.I.R., in whose hands it now is.

In attempting a review of progress made since the initiation of the investigation, certain difficulties have to be recognised. We are not in the position of having uniformly distributed observation stations over the whole country, but there is rather a tendency to concentrate stations in the more highly polluted neighbourhoods. This is a perfectly natural result since such places are likely to be more concerned with the condition of their atmosphere than would be, for example, a sea-side resort far removed from any manufacturing area. However, one effect of this is that when attempting to estimate the condition of the air of this country as affected by smoke pollution, allowance has to be made for this concentration. One way of examining the changes which have occurred would be to take each station individually and compare the result obtained year by year, and this in some respects is the most satisfactory. In the case of large cities where a number of stations have been established, the average of the stations may be taken and, provided they retain the same position, may be compared with a view to finding what improvement, if any, has resulted.

In this paper the details of the methods adopted for measurement will not be dealt with, but rather the general results obtained. It may, however, be stated briefly that the measurement upon which most reliance is based is an estimation of the weight of matter deposited from

the air upon a measured area at or near ground level. A standard deposit gauge has been evolved for this purpose and is in use at about 100 different stations throughout the country.

In addition to the measurement of deposit, the suspended matter is also examined by a different method, *i.e.* by filtration through white paper leaving a stain which, in smoke-polluted cities, can be made to give a measure of the degree of pollution of the air by sooty matter.

The desirability of reviewing the progress made to date will be evident since it will be seen from what follows that the rate of improvement of the air of our cities is by no means as great as it should be, and the author hopes that the condition set forth in this paper will make it evident that greater efforts must be made in the direction of smoke abatement if we are to obtain any marked and continued improvement.

Since this investigation started there have been in operation 158 stations making official reports. These, however, have not all been in operation at the same time, nor have they all continued from the beginning until now. Hence it becomes necessary to make some selection of stations in examining the variation of the deposit. This has been done by excluding from the comparison any station with less than eight consecutive years' observations, except in one or two exceptional instances.

The reports made of deposited impurity show this analysed into soluble and insoluble matter, and experience has shown that the amount of rainfall in any year has a marked effect upon the amount of soluble matter deposited, but little effect upon the insoluble. Hence we must not compare individual years but rather find some method which will show the trend over a longer period of years. Again the insoluble matter deposited has been divided into tar, carbonaceous matter and ash, and the soluble into loss on ignition and ash, while the soluble matter has also had the amount of sulphates, chlorine and ammonia estimated.

In such an examination as this and in order not to burden the paper with too many figures it is advisable to select a few of the more important elements of the deposit for consideration. It has, therefore, been decided to compare upon the basis of total solids deposited from the atmosphere in any year, the deposit of sulphates found in the soluble matter and the amount of tar deposited. Before dealing with the individual stations, it might be well to give the reasons for this selection :—

The total solids deposited gives a gross measure of the pollution reaching the ground from the air, although it is not all derived from the smoke or grit from chimneys, it may at least be regarded as atmospheric pollution. Some of the deposited matter is undoubtedly derived from wind-blown dust, and hence it is found that the insoluble part of the deposit tends to be higher in summer than in winter, whereas the soluble part tends to be higher in winter than in summer.

The selection of sulphates deposited is based upon the fact that the main source of pollution of the atmosphere by sulphur is from the combustion of fuel containing sulphur. In addition, it is one of the most dangerous products and is injurious to health and vegetation as well as to building material ; while, being derived from the combustion of fuel, it is some measure of the pollution from this source. Unfortunately the sulphate emitted from a chimney is in an invisible form and is, therefore, not eliminated by eliminating visible smoke. It follows also that efforts to attack visible smoke do not necessarily reduce the amount of sulphur pollution in the air, and it has to be dealt with independently by some of the methods recently adopted successfully in our large power stations.

Tar is pre-eminently a product of bituminous coal burnt in domestic

fires. Hence it is included as some measure of the degree of pollution by domestic smoke. It is well known that the soot from domestic smoke contains a high percentage of tar, often up to 30 per cent., whereas that from boiler furnaces or other well designed furnaces contains little or no tar.

The above reasons will explain why these three elements of pollution have been selected to give a reasonable measure of the progress made in the prevention of pollution of the air.

The stations examined are shown in the tables below for the years available and a brief summary of the position may now be given referring to the attached tables :—

In dealing with the progress of events, it will be best to take individual cities because the conditions in different cities vary very much, and it will be observed from the tables that, whereas in some cases there has been improvement, in others this is not the case.

London.—In this case the figures shown are an average for eight stations, and, as in all other tables, they represent the deposit from the air estimated in English tons per square mile. We have here a consecutive series of twenty years with no break, and these should give a very fair picture of the course of events. Starting at 1915/16 we find the deposit of total solid matter was 415 tons per square mile, 72 tons of sulphates and 4 tons of tar. Following this there was a fairly steady improvement until 1921/22, that is for seven years, and this improvement shows up as a reduction in total deposit and in deposit of sulphates. In this year 1921/22 the total deposit had fallen to 284 tons per square mile and the sulphates to 25 tons. In the following years between 1921 and 1935, the total deposit has altered very little, there have been some ups and downs, but it would not be very wrong to say that the conditions have remained practically unaltered. It is not quite so satisfactory when we look at the sulphates deposited, as here we find actually an increase, although not very great. So that while in 1921/22 there was a deposit of 25 tons, in 1934/35 this had increased to 49 tons per square mile, while tar remained unchanged. Here then we find a state of affairs which is not very easy to explain, but at any rate it can be said that there is no great ground for optimism as regards the condition of the air of London during the last fourteen or fifteen years.

Glasgow.—Here also we have an unbroken series of twenty years' observations, and the figures are an average of nine stations. In some respects it follows curiously the behaviour of London. In 1915/16 the total deposit was 422 tons per square mile, 92 tons of sulphates and 4 tons of tar. This diminished regularly until 1921/22 when we find a total deposit of 255 tons, and 34 tons of sulphates per square mile. Since then for the next fourteen years there have been some ups and downs but no general improvement can be observed. In 1934/35 the total deposit was 268 tons per square mile including 37 tons of sulphates, while tar remained unchanged.

The cause of this curious behaviour in the two cities is not by any means obvious, and may be a suitable subject for speculation and discussion at a meeting such as this.

Wakefield, W.R. Rivers Board.—This gauge is in the centre of the city in a manufacturing and residential area. There is a period of eleven years with one or two breaks which do not affect the sequence very much, and, so far as total deposit from the air and the deposit of sulphates are concerned, Wakefield shows a continuous improvement. The deposit in 1924/25, the first year available, amounted to 613 tons per square mile, while sulphates amounted to 136 tons and tar 8 tons. In 1934/35 this was reduced to 225 tons per square mile total deposit, 24 tons sulphates and 6 tons tar, a very creditable state of affairs.

Bournville Works.—This gauge is 4 miles S.W. by S. of Birmingham. There are ten years' consecutive records and a fairly constant history of

improvement, but not anything very spectacular. Starting in 1924/25 with 192 tons per square mile of total deposit, 17 tons of sulphates and 2 tons of tar, we finish in 1934/35 with 173 tons of total deposit, 18 tons of sulphates and 1 ton of tar.

Bournville Village.—This gauge is 4½ miles S.W. of Birmingham in a residential area. Here we have nine years' records, and a slight improvement is also indicated. In 1925/26 the total deposit amounted to 157 tons per square mile, the sulphates to 18 tons and the tar to 1 ton, while in 1933/34 the figures had fallen to 93 tons per square mile of total deposit, 11 tons of sulphates and 1 ton of tar. This behaviour is somewhat similar to that of Bournville Works, it shows an improvement but not a very great one.

Birmingham Central.—There are ten years' records and again a history of improvement, but not very great. Starting in 1922/23 with a total deposit of 419 tons per square mile, sulphates 50 tons and tar 4 tons, we finish in 1931/32 with 340 tons per square mile of total deposit, 27 tons of sulphates and 4 tons of tar. This is a somewhat similar history to the Bournville records. This is for the centre of the city.

Cardiff.—This gauge is also in the centre of the city. We have nine years available at Cardiff, commencing at 1926/27 with a total deposit of 368 tons per square mile, sulphates 21 tons and tar 9 tons. This improved until 1930/31 when there was 133 tons total deposit, 22 tons of sulphates and 2 tons of tar. After that the improvement was not maintained, but with some ups and downs we arrive at 140 tons per square mile total deposit, 17 tons of sulphates and 1 ton of tar in 1934/35.

Gloucester.—This shows a fairly constant improvement for the nine years of which we possess records. It commences in 1926/27 with 343 tons per square mile total deposit and finishes in 1934/35 with 117 tons per square mile. In this case we have no record of sulphates or tar.

Leicester, Town Hall.—This gauge is less than ¼ mile S.S.E. of the centre of the city. There are only eight years' records here, commencing in 1927/28 with 379 tons per square mile total deposit, 42 tons sulphates and 3 tons tar. There was very little improvement noticeable until 1933/34 when there was a definite drop in the deposit, and in 1934/35 the total deposit amounted to 259 tons per square mile, sulphates 24 tons and tar 4 tons. We may rank this city as having improved at any rate during the last couple of years.

Newcastle, Westgate.—The gauge is approximately ¾ mile west of the centre of the city. We have ten years' observations commencing 1925/26, and a fairly constant history of improvement up to 1934/35. The total deposit amounted to 443 tons per square mile, the sulphates 69 tons and the tar 13 tons in 1925/26 ; these figures had fallen to 292 tons total deposit, 35 tons sulphates and 8 tons tar in 1934/35.

Newcastle, Town Moor.—This gauge is 1½ miles north of the centre of the city in fairly open country. It has the same series of years and shows a somewhat similar history to that at Westgate, but not such a marked improvement. The total deposit in 1925/26 was 268 tons per square mile, the sulphates 45 tons and the tar 4 tons, while in 1934/35 these figures had dropped to 236 tons per square mile total deposit, 42 tons sulphates and 6 tons tar.

Rothamsted.—This gauge is 1 mile S.W. of Harpenden Town in open country in a residential district. Rothamsted is a country station which gets most of its pollution by drift from London or other cities. There are sixteen years' observations, and a definite improvement during this period although not a very constant one. In fact most of the improvement occurred in the first four years when the deposit fell from 245 tons in 1919/20 to 86 tons per square mile in 1922/23. There were ups and downs after this until 1934/35 when the total deposit was 83 tons per square mile. We may, therefore, say that the last twelve years show practically no improvement.

Rochdale, Technical School.—Here we have twelve records covering the years 1916/17 to 1927/28, and there is, on the whole, an evidence of reduction of deposit based upon the total solids. Starting in 1916/17 with 731 tons per square mile, we finish in 1927/28 with 584 tons.

To continue with the story of Rochdale, as the Technical School gauge did not continue beyond 1927/28, we have to use the records from another gauge, *i.e.* at the Town Hall, and while these figures must not be taken as representing the same conditions as held at the Technical School, they may be compared amongst themselves for improvement or otherwise. In the Technical School gauge the observations of sulphates and tar were not carried out, but these were estimated in the Town Hall gauge.

Rochdale, Town Hall.—This gauge is in the centre of a manufacturing city. We have a period of eight consecutive years' observations here, and if we base our conclusions on total solids the deposit drops from 350 tons per square mile in 1927/28 to 236 tons in 1934/35. The sulphates and tar, however, do not tell quite the same story, and as these are specifically combustion products, they are perhaps more reliable. Thus in 1927/28 there was a deposit of 38 tons of sulphates per square mile, and 4 tons of tar, while in 1934/35 the respective figures were 46 and 4, showing no improvement.

Burnley, Town Hall.—There are nine years' observations available here, and the station is very remarkable in the sense that a sudden improvement occurred after three years, and the low level was maintained subsequently. In 1925/26 the total deposit amounted to 869 tons per square mile, 117 tons of sulphates and 25 tons of tar. In 1927/28 the figures were respectively 856, 137 and 11. There was a sudden drop next year to a total deposit of 464 tons per square mile, sulphates 31 tons and tar 10 tons, and the condition remained more or less the same as regards total solids and sulphates until 1933/34, the final figures being total solids 427 tons per square mile and sulphates 31 tons. There was, however, a definite increase in the quantity of tar deposited, which, increased steadily up to 30 tons per square mile in 1933/34, an excessively heavy deposit. There is no obvious explanation of the sudden reduction in the amount of deposit, but the fact that it occurred simultaneously in the total solids and in the sulphates suggests that there was a definite reduction in the amount of smoke. This gauge is in the centre of the city in a manufacturing district.

The cities which show at least some improvement in the amount of deposit from the air have been dealt with first, and we will now examine those which show no improvement or a falling back.

Leeds, Headingley.—The gauge is in a residential area 3 miles from the centre of the city. We have twelve years of observations, and the history is not one of continuous improvement, but rather the reverse. Commencing in 1923/24 with 72 tons total deposit, 13 tons sulphates and 1 ton per square mile of tar, we finish in 1934/35 with 122 tons per square mile total deposit, 14 tons sulphates and 1 ton tar.

Leeds, Hunslet.—This gauge is in an industrial area 1½ miles from the centre of the city. Here again we have thirteen years' records and somewhat the same story. There is practically no difference between the condition now and twelve or thirteen years ago. In 1922/23 the total deposit amounted to 305 tons per square mile, the sulphates to 25 tons and the tar to 5 tons. In 1934/35 the figures were 301 tons of total deposit, 23 tons of sulphates and 3 tons of tar per square mile.

Leeds, Park Square.—The gauge is ¼ mile from the centre of the city in a densely populated area. There are thirteen years' observations available, commencing 1922/23 when the total deposit was 305 tons per square mile, sulphates 29 tons and tar 5 tons. These figures have altered very little until 1934/35 when the total deposit amounted to 338 tons per square mile, the sulphates to 23 tons and the tar to 3 tons. Thus in the total impurities deposited in the air we find no improvement, but there is a slight improvement in the sulphates and tar.

Leeds, York Road.—This gauge is 1 mile from the centre of the city in a densely populated working-class district. Here we have twelve years' observations and the figures tell the same story as at Park Square. Commencing 1923/24 with a total deposit of 247 tons per square mile, 25 tons of sulphates and 3 tons of tar, we finish in 1934/35 with 292 tons of total deposit, 24 tons of sulphates and 4 tons of tar. Thus these stations in Leeds indicate no improvement in the condition of the atmosphere.

Liverpool, Netherfield Road.—The gauge is 1½ miles N.N.E. of the Town Hall in a manufacturing and very thickly populated area. There are fourteen years' observations, starting in 1921/22 when the total deposit was 548 tons per square mile, sulphates 52 tons and tar 4 tons. Conditions have not improved since then, in fact there is evidently more pollution in the atmosphere, since the total deposit in 1934/35 was 590 tons per square mile, sulphates 66 tons and tar 5 tons.

Marple.—This gauge is in open country tending to become suburbanised. We have eleven years' observations at Marple commencing in 1924/25 with a total deposit of 102 tons per square mile, 38 tons of sulphates and 2 tons of tar. The total deposit shows no improvement during the following ten years, but sulphates and tar do show a reduction. The figures for 1934/35 were 105 tons per square mile of total deposit, 21 tons of sulphates and 1 ton of tar.

St. Helens.—The gauge is in the centre of the city. We have eighteen years' consecutive observations here commencing 1917/18 with 612 tons per square mile total deposit, 99 tons of sulphates and 13 tons of tar. These figures fell rapidly during the subsequent three years, and in 1920/21 the total deposit was 371 tons per square mile, the sulphates 59 tons and the tar 4 tons. After that the improvement was not maintained, but in some years, the conditions went back and in 1934/35 the total deposit amounted to 431 tons per square mile, sulphates 30 tons and tar 9 tons. Looking at the column of sulphates deposited here there is a period from 1927/28 to 1934/35 when there was a continuous reduction in the sulphates, this was not, however, reflected in the tar or total deposit.

Stoke-on-Trent, Leek Road.—This gauge is in the centre of the city in a manufacturing area. We have available eleven years' observations commencing 1924/25 and the position disclosed is not very satisfactory. In 1924/25 the deposit of total solids was 192 tons per square mile with 21 tons sulphates, while in 1934/35 this had risen to 232 tons of total deposit and 29 tons of sulphates. As will be seen there has been a gradual deterioration, not entirely continuous.

At Castleford, Garston and Edinburgh, where there are not a great number of years for comparison, the indications are of a fairly steady condition of impurity. There are slight variations from year to year, but hardly anything which can be regarded as evidence of improvement or deterioration.

We could thus divide the stations referred to in this paper into three groups, the first in which a definite improvement has been indicated in the degree of pollution of the air. This group includes London, Glasgow, Wakefield (W.R. Rivers Board), Bournville Works and Village, Birmingham Central, Cardiff, Gloucester, Leicester Town Hall, Newcastle (Westgate and Town Moor), Rothamsted, Rochdale (Technical School and Town Hall), and Burnley. In the second group there has been an equally definite deterioration. This group includes, Leeds (Headingley, Hunslet, Park Square and York Road), Liverpool (Netherfield Road), Marple, St. Helens, and Stoke-on-Trent (Leek Road), while the third group shows little or no change in the condition of the air and includes Castleford, Garston and Edinburgh.

It is necessary to remember that a certain selection has had to be made of the available stations for reference in this paper. It is hardly possible to give a definite answer to the general question " Is the

TABLES SHOWING THE AMOUNT OF IMPURITY DEPOSITED IN TONS PER SQUARE MILE (ANNUAL TOTAL).

Glasgow (Average of nine stations).				Liverpool, Netherfield Road.				London (Average of eight stations).			
Year.	Total Solids.	Sulphates.	Tar.	Year.	Total Solids.	Sulphates.	Tar.	Year.	Total Solids.	Sulphates.	Tar.
1915/16	422	92	4	1921/22	548	52	4	1915/16	415	72	4
1916/17	380	89	4	1922/23	625	50	6	1916/17	400	68	4
1917/18	447	84	7	1923/24	645	61	7	1917/18	379	60	3
1918/19	386	77	3	1924/25	577	63	7	1918/19	372	70	3
1919/20	316	59	2	1925/26	635	78	6	1919/20	346	53	3
1920/21	322	42	5	1926/27	547	72	5	1920/21	307	27	5
1921/22	255	34	3	1927/28	557	70	6	1921/22	284	25	5
1922/23	254	38	2	1928/29	636	65	5	1922/23	302	36	3
1923/24	321	41	3	1929/30	552	64	7	1923/24	288	33	2
1924/25	284	51	3	1930/31	520	67	6	1924/25	319	41	3
1925/26	274	46	3	1931/32	520	70	6	1925/26	264	32	3
1926/27	284	43	3	1932/33	585	61	5	1926/27	303	40	4
1927/28	320	50	2	1933/34	522	53	5	1927/28	316	40	4
1928/29	263	38	2	1934/35	590	66	5	1928/29	255	29	4
1929/30	280	41	3	1935/36	683	57	6	1929/30	272	35	4
1930/31	278	39	3					1930/31	289	41	4
1931/32	252	37	2					1931/32	281	41	4
1932/33	232	33	2					1932/33	272	41	4
1933/34	230	27	4					1933/34	315	45	5
1934/35	268	37	3					1934/35	298	49	5
1934/36	239	28	3					1935/36	284	43	4

condition as to smoke pollution improving in this country or otherwise." It will be seen from what has already been said that improvement may be going on in one place and deterioration in another, and it would not be fair, for example, to take two such places and by averaging them conclude that the general condition was unaltered. It is true that the smoke emitted in any city is not confined to its own boundaries, but spreads over the whole country, and in this sense there is a general pollution of the air which might be estimated as distinct from the local pollution produced in a specific neighbourhood. Possibly the condition of Garston might be taken as representing this general rather than local pollution, since the station is situated well out in the country and produces little smoke pollution in its own neighbourhood.

The lesson to be learnt from the foregoing is fairly obvious: The fact that certain cities have reduced the pollution of their air very much is proof that it can be done with care and attention, and might be given as an answer to any doubts raised by other cities as to their ability to reduce smoke. The condition in this country at present is by no means satisfactory, and it is obvious that we should put a great deal more energy and effort into smoke prevention than we are doing. This might be taken as the lesson to be learnt from the cities of groups two and three. It is, however, not the cities only which suffer from the smoke pollution: it is astonishing the degree of pollution of the air in the open country to leeward of a great city such as London. The track of the smoke cloud extends for many miles down wind and the concentration of smoke is so great even in the open country under such conditions that far more attention should be given to it by Public Health Authorities. The

author has often experienced a dense smoke haze, easily visible in a room, at a distance of 12 miles S.W. of London. Given suitable conditions which impede the dispersion of the smoke cloud from the city, that is, a low wind velocity and an inversion of the vertical temperature gradient overhead, then the smoke drifts along with little reduction in its concentration. The author has seen on the coast of Devonshire a thick smoke haze through which the sun had a deep orange colour, and he has traced this haze to the manufacturing districts in the Midlands. This paper is, however, intended to be rather a review of progress since the beginning of the investigation than a pointing out of lessons, and indeed they are sufficiently obvious to need little indication.

GENERAL DISCUSSION.

Mr. C. F. Goodeve (*London*) said : In welcoming us to Leeds the Vice-Chancellor of this University expressed a hope that we would close our discussion in a happier frame of mind than we had commenced it and that, before many years, we would do something to relieve the irritations of housewives, etc. From the title of this paper one receives a certain amount of encouragement, but it is misleading. This adequate summary given by Dr. Owens shows conclusively that, except for a few cities during the five-year period from 1915, no reduction in any of the impurities deposited from the air has been found and, in a good many cases, there is a serious increase.

An important question for the consideration of this meeting is " What is being done, or what is proposed to be done, with regard to the situation ? " We have an active society which carries on extensive propaganda work. We can only hope that it will receive increased support and that its efforts may produce some improvement.

There is also " The Atmospheric Pollution Research Committee." Their very interesting annual reports contain, amongst other things, the results of an enormous number of determinations of the deposits from the air in different cities in this country. The available statistics now cover millions of observations. Some years ago, I attempted to make a statistical analysis of these figures. Beyond showing what Dr. Owens has discussed in this paper, the results of this analysis were disappointing. Mr. Wilsdon, however, has persevered further and obtained a number of curves which are given in the last Report. In this connection, I should like to quote from his paper the following sentence (p. 51) :—

" Whatever may be the true interpretation of the early data, it does not seem possible to advance much further by examination of existing records."

It would appear that Mr. Wilsdon agrees with me that the large amount of work involved in obtaining these statistics is not leading to any definite conclusions. These figures cover a period of twenty-one years. I would ask the members of this committee, most of whom are present, seriously to consider whether it is possible to direct some of the enormous amount of labour involved in obtaining these statistics along more useful lines.

I am not familiar with the terms of reference under which this committee is appointed, but I would venture to suggest that they might find practical means to help the situation by, for example, advising local authorities or even investigating for them the causes of atmospheric pollution. One finds in the reports for a number of years that unusually high deposits were found in the neighbourhood of Ravenscourt Park, London. I would like to ask the committee whether the cause of this high deposit was ever found and if so, were any steps taken to remove it.

The most encouraging aspect of the whole question comes from the amount of independent work which is being done by private companies for the improvement of atmospheric pollution. The London Power Company are among the pioneers in this work. When one considers the large amount of private consumption of coal which will be replaced by electricity produced from a practically pollution-free power station, one can appreciate that the Battersea Power Station will produce no small improvement in the conditions obtaining in London. In this connection, I would like to quote from Dr. Coste's paper to this discussion :

"Dust from leaves in Battersea Park, near the Power Station, was mostly domestic and horticultural in origin, very few spheres being found, showing the efficiency of the gas-washing plant."

In addition to the work of the London Power Company, there are also the highly successful experiments of Imperial Chemical Industries carried out at Billingham and described in Nonhebel's paper to this discussion. As a result of their work it is now possible to instal an efficient plant for the smallest of industrial chimneys. There remains no excuse for the pollution of the atmosphere by the small factory.

We all look forward to the opening of the Fulham Power Station in London and feel confident that it will be as successful as the others. There are also a considerable number of gas washing plants for power stations in various parts of the country, but the small factory is very slow in responding.

Aside from this independent work, we have little to satisfy our minds as to the future. Chemistry and engineering have solved most of the practical problems involved and the matter is now largely a political one. It is to be hoped that the civic authorities in this city will take a leading part and, before long, Leeds will lose its title of "The City of Perpetual Mourning."

Professor F. G. Donnan (*London*) said he thought that Mr. Goodeve's criticisms were unjustified. The Atmospheric Pollution Committee had done an immense amount of excellent work in devising methods of measurement and obtaining quantitative data. They could not be blamed for any failure on the part of Municipal and Government Authorities to take action.

Dr R. Lessing (*London*) pleaded for a survey of the sources of atmospheric pollution as distinct from the observation of the incidence and effects. For this purpose, a limited number of types of coal-consuming plants and appliances should be investigated. Whilst the total emission may not have been reduced in amount in the 20 years during which observations have been made, the character had changed, mainly in the direction of a diminishing soot and tar content and an increasing proportion of ash dust and coke particles.

Dr. G. M. B. Dobson (*Oxford*) said : As I have some responsibility for the work of the Atmospheric Pollution Research Committee, I should like to make some explanations in view of Mr. Goodeve's friendly criticisms of this work.

Firstly, it is entirely outside the scope of this Committee to initiate work on methods of reduction of smoke from either domestic or factory chimneys, or to test existing methods. Their work is to devise methods for the accurate measurement of the pollution existing in the air, and to advise local authorities of the best methods they should use in measuring the pollution in their towns. It is not even the duty of the Committee to make the routine observations of pollution all over the Kingdom, this being the duty of Local Authorities. In certain special cases the Committee do make observations, but their small income would have to be multiplied many times if they were to be responsible for all the observations now being made by the local authorities.

The Committee are responsible for advising what type of pollution should be measured, and it is entirely due to them that the method of measuring gaseous SO_2 was worked out by the Government chemist at

their special request, and at the expense of their funds. In this connection I would also mention that the question of the possible presence of droplets of H_2SO_4 has been much discussed by them, and the work which Mr. Coste (a member of the Research Committee) reported to this Conference, is a direct result of this. So far as I know, this is the first time an accurate measurement of the amount of H_2SO_4 in city air has been made, and the suggestion that a method had been worked out by the Government chemist several years ago but not used by the Committee is not correct.

Mr. G. Nonhebel (*Billingham*) said : The higher deposits of sulphates in Central London may well be due to the increasing use of coke for central heating in the office districts. Coke contains more sulphur in relation to its calorific value than coal, and the coal used for coking has usually in any case a higher sulphur content than best quality domestic coal.

With the growth of large centrally situated power stations there is now a strong case for the use of low pressure pass-out steam for heating in densely populated areas (particularly in towns like Leeds, where the domestic smoke from closely packed houses, often back to back, is so serious in the valleys) and close to one of the power stations. By this means a large proportion of the latent heat of the steam which is now lost in the condenser water would be saved.

For such a scheme to be tried, it would really be necessary to have a State-aided large-scale experiment, and to forbid the use of open fires in the district under investigation.

In New York City one of the central heating stations has a boiler output of 500 tons/hour. The visibility in this city is generally far better than that in London, owing to the absence of open domestic fires. The main problems there are, however, the elimination of grit and SO_2 from the chimneys of the large power stations, particularly in the Tudor City district where many of the buildings tower above the chimneys of two large power stations.

Dr. J. S. Owens (*London*), in reply (*communicated*) : In reply to Mr. Goodeve's remarks, I would first refer to his last paragraph, in which he says that " chemistry and engineering have solved most of the practical problems involved and the matter is now largely a political one." This is really the heart of the whole question. If I might paraphrase Mr. Goodeve's statement, I would put it in this form : " So far as the prevention of smoke pollution from industrial processes is concerned, we are in a position to prevent this if we want to, and the continued existence of a polluted atmosphere from this cause is evidence of the lack of a sufficiently strong public desire to prevent it." This brings me to the suggestions as to the work of research on atmospheric pollution. I do not agree with Mr. Goodeve that the statistics obtained are not leading to any definite conclusion. The work done has shown clearly the degree of pollution of the air and the improvement which can, and has been affected in certain places. It will, I think, be generally accepted that if a problem like this is to be tackled, the first essential is some means of measuring, both to enable us to realise the extent of the evil and to indicate the degree of success attending efforts made to reduce it. The title usually applied to the work, that is " The Investigation of Atmospheric Pollution," is perhaps a little vague as to the specific nature of the investigation intended. The object in view was strictly one of measurement. Of course, this does not invalidate any criticism such as that another object should have been included, or might still be included, but the particular problem attacked was quite sufficient in view of the funds available.

In reply to the query as to the heavy deposits in Ravenscourt Park, London, the exact source of these deposits has not been found, nor have the Committee initiated any steps to remove it. This is a case, where such action would be outside the terms of reference of the Committee.

THE INFLAMMATION OF DUST CLOUDS.

By R. V. Wheeler.

A cloud of fine dust in air behaves in many respects similarly to a gas or vapour. If the dust is inflammable, its similarity to a gas in behaviour extends to its ability to propagate flame if it is present in sufficient concentration in the air.

Dusts vary in their degree of " inflammability " (*i.e.* in their ability to propagate flame when they form clouds in air) with their chemical composition and their fineness. It is not so easy to obtain a direct measure of the inflammability of a dust as it is of a gas or vapour. It is not easy, for example, to determine accurately the dilution limits (lower and upper) such as are usually sufficient to define the inflammability of a gas or vapour.

An indirect measure of the inflammability of a dust can be obtained by making use of the fact that the admixture with it of a sufficient quantity of an incombustible dust (stone dust) can render it incapable of propagating flame. Such a measure has been used more particularly for assessing the relative inflammability of coal dusts, mainly because a practical method of rendering harmless the dust produced during coal-mining is to treat it with stone dust. Two examples of the problems studied regarding the inflammability of coal dusts will be considered : (1) The effect of the concentration of the dust (of constant composition and fineness) ; and (2) the effect of the fineness of the dust (of constant composition and concentration).

The Effect of the Concentration of the Dust on its Inflammability.

The method of experiment used was, briefly, to determine the amounts of a chosen stone dust, intimately mixed with the coal dust and of the same degree of fineness, required just to prevent the continued propagation of flame when the mixtures were strewn along an explosion gallery and ignited by a standard source of ignition.

The explosion gallery was constructed of steel tubing 4 ft. in diameter, and was 325 ft. long. It was closed at one end. A known quantity of an intimate mixture of coal dust and stone dust (Fuller's Earth), prepared by hand from materials pulverised so that between 80 and 85 per cent. could pass through a 200-mesh (I.M.M. standard) sieve,* was spread evenly on the floor of the gallery. The means of ignition was a blown-out shot of 20 oz. of gunpowder, tightly stemmed with 8 in. (1. lb.) of coal dust. The shot was fired from a small cannon with a 2-in. bore placed on the floor of the gallery at a distance of 15 ft. from the closed end, with its muzzle pointing towards the open end. An open-ended steel tube, 1 ft. in diameter and 6 ft. long, was arranged immediately in front of, and in line with, the cannon. A quantity of the dust mixture to be tested, such that there were $1\frac{1}{2}$ lb. of coal dust (irrespective of the proportions of coal dust and stone dust in the mixture), was strewn evenly within this tube.

* Throughout this paper, the meshes of sieves referred to are I.M.M. standard.

A series of tests with a number of loadings of a chosen coal dust was made, different proportions of stone dust being used at each loading until two mixtures were found of which one propagated flame throughout the gallery and the other, containing $2\frac{1}{2}$ per cent. more stone dust, merely extended the flame of the cannon-shot by 75 to 175 ft.

The results of crucial experiments with a coal dust of average inflammability are recorded in Table I.

TABLE I.--THE EFFECT OF THE CONCENTRATION OF COAL DUST ON ITS INFLAMMABILITY.

Expt. No.	Composition of Mixture per Cent.		Concentration in Gallery (oz. per cu. ft. of gas).		Result Length of Flame.
	Coal Dust.	Stone Dust.	Mixed Dusts.	Coal Dust.	
716	40	60	0·60	0·24	75 ft.
748	40	60	0·65	0·26	75 ft.
724	42·5	57·5	0·50	0·21	75 ft.
746	42·5	57·5	0·50	0·21	75 ft.
723	42·5	57·5	0·55	0·23	Throughout
715	42·5	57·5	0·60	0·255	Throughout
720	42·5	57·5	0·65	0·28	Throughout
719	42·5	57·5	0·70	0·30	125 ft.
747	42·5	57·5	0·70	0·30	175 ft.
727	45	55	0·90	0·405	Throughout
729	45	55	1·00	0·45	150 ft.
754	45	55	1·00	0·45	125 ft.
750	47·5	52·5	1·55	0·74	Throughout
752	47·5	52·5	2·20	1·045	Throughout
753	47·5	52·5	3·00	1·425	Throughout
731	50	50	0·30	0·15	100 ft.
744	50	50	0·30	0·15	75 ft.
738	50	50	0·35	0·175	Throughout
742	100	nil	—	0·05	125 ft.
743	100	nil	—	0·05	150 ft.
739	100	nil	—	0·075	Throughout

For the concentrations of dust recorded in this table in ounces per cubic foot capacity of the gallery, the assumption is made that all the dust strewn on the floor of the gallery was raised in suspension in the air either by the concussion produced by the cannon-shot or during the subsequent propagation of flame. The results are shown graphically in Fig. 1. The " upper limit " of concentration for this coal dust was not obtained. No experiments were made with concentrations of coal dust higher than 1·425 oz. per cubic foot of air. This concentration, for a mixture containing 52·5 per cent. of stone dust, amounts to about $2\frac{1}{2}$ lb. of mixture per linear foot of the gallery and such quantities as would be required to reach the upper limit, judging by the slope of the curve in Fig. 1, would have presented considerable obstruction in the gallery.

During an experiment in which the loading of dust along the gallery was initially heavy, the concentration of dust in the air was probably neither initially uniform nor continuously maintained as the flame travelled but was affected by the degree of turbulence created ahead of the flame. The initial inflammation might raise the whole of the dust as a dust cloud and the flame, after travelling a short distance, might begin to slacken speed by reason of the cooling action of the large excess of dust. The checking of the flame in this manner would reduce the amount of turbulence ahead of it and much of the dust would fall out of suspension in the air, leaving a concentration more favourable to the propagation of

flame. It was noted that the progress of flame along the gallery when it had been heavily loaded with dust was slow and spasmodic.

The " lower limit " of concentration of this coal dust (under the conditions of test) was about 0·07 oz. per cubic foot of air, and the optimum concentration, which was sharply defined, was 0·23 oz.

INFLAMMATION   CONTINUED.   ●
INFLAMMATION   SUPPRESSED.   ○

| 0 | 0·2 | 0·4 | 0·6 | 0·8 | 1·0 | 1·2 | 1·4 | 1·6 |

CONCENTRATION OF COAL DUST IN THE GALLERY – OUNCES PER CUBIC FOOT OF AIR.
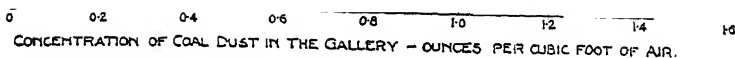
FIG. 1.—The effect on its inflammability of the concentration of coal dust in air.

With a coal dust of low inflammability by reason of its chemical composition, the amount of stone dust required to suppress inflammation, even at the optimum concentration, is small. Such a coal dust was therefore used in a series of experiments designed to test the possibility of determining an upper limit of concentration. The results are recorded in Fig. 2.
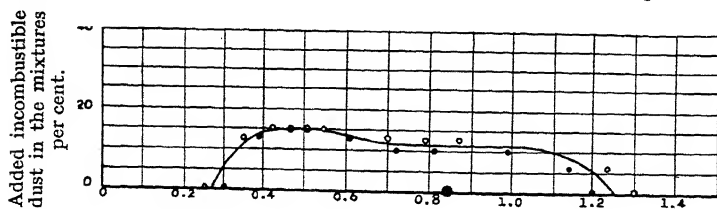
Concentration of coal dust in the gallery (ounces per cubic foot of air space).

FIG. 2.—The effect on its inflammability of the concentration of coal dust in air.

An analogy can be drawn between these experiments and gaseous inflammations. Thus, Coward and Hartwell [1] have determined the limit of inflammability of firedamp in atmospheres containing carbon dioxide. Their results are shown graphically in Fig. 3, where the concentration of methane in the air is plotted against the concentration of carbon dioxide required to suppress inflammation. The concentrations of the gases are expressed as percentages by volume.

[1] *Safety in Mines Research Board Paper*, No. 19.

The Effect of the Fineness of the Dust on its Inflammability.

The physical quantity that measures the fineness of a particle of coal dust most significantly with respect to its reactivity, and thus with respect to its inflammability, is its specific surface, *i.e.* the ratio of its surface to its mass. Sufficiently accurate (relative) values for the specific surface of coal dust samples can be decided from their sieving analyses, whereby the proportions of particles of different sizes are measured.

Concentration of methane in the air—per cent.
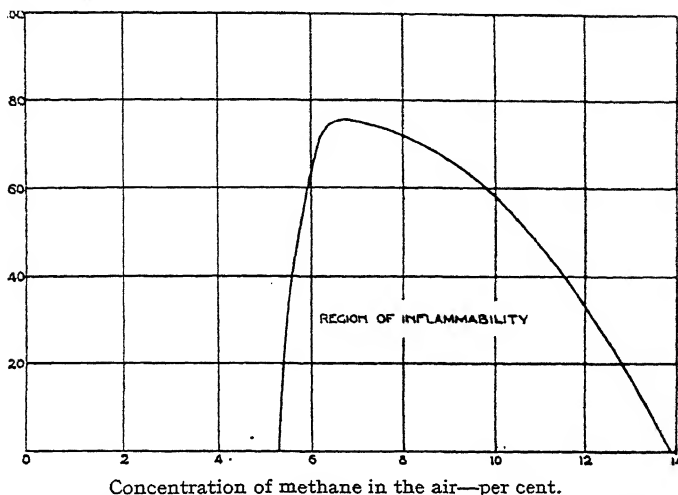
Fig. 3.—The effect on its inflammability of the concentration of methane in air.

Tests of the effect of the fineness of a coal dust on its inflammability were made in a similar manner to those on the effect of its concentration, using a coal which was as inflammable (by reason of its chemical composition) as that used for the experiments recorded in Table I. The stone dust used was, as before, Fuller's Earth, 85 per cent. of which would pass through a 200-mesh sieve, and all the tests were made with the optimum concentration of coal dust.

TABLE II.—THE EFFECT OF THE FINENESS OF COAL DUST ON ITS INFLAMMA-BILITY.

Preparation.	Sieving Analysis, per Cent.							Index of Inflammability.	
	3-5.	5-8.	8-20.	20-50.	50-100.	100-200.	Through 200.	Stone Dust, S, per Cent.	Ratio 100/(100−S).
A.	—	—	—	—	1	14	85	62·5	2·67
B.	3	7	6	4	2	13	65	55	2·22
C.	—	—	3	16	23	22	36	50	2·00
D.	—	—	4	33	13	14	36	45	1·82
E.	8	17	13	10	4	10	38	42·5	1·74
F.	—	—	29	21	7	11	32	40	1·67
G.	—	—	40	29	11	9	11	17·5	1·21
H.	8	22	24	19	8	7	12	15	1·18
J.	12	29	23	16	6	6	8	5	1·05

Nine preparations of the coal were made, to provide dusts of different degrees of fineness, by the use of coarse and fine grinding in different mills and by blending the products.   Table II. records sieving analyses of these preparations, together with their " inflammabilities " expressed (*a*) as percentages of stone dust, *S*, in the mixtures through which (at optimum concentration) flame just failed to propagate when tested in the explosion

TABLE III.—FINENESS FACTORS FOR SIEVED FRACTIONS OF COAL DUST.

Mesh of Sieve.	Width of Mesh. Inch.	Mean Diameter of Particle (*D*). Inch.	Fineness Factor, $\left(\dfrac{0.00375}{D}\right)$.
3	0·1667		
5	0·1000	0·1333	0·028
8	0·0625	0·0813	0·046
20	0·0250	0·0438	0·086
50	0·0100	0·0175	0·214
100	0·0050	0·0075	0·500
200	0·0025	0·00375	1·000

gallery, and (*b*) as the ratios $100/(100 - S)$, which show the amounts of mixed coal dust and stone dust which unit quantity of coal dust just failed to render inflammable.   The use of the latter index greatly simplifies discussion of the relationship between fineness and inflammability.

From general inspection of Table II. it is evident that the inflammability of a coal dust is affected in a marked degree by the proportion of through 200-mesh dust that it contains.   The results of the tests with Preparations G, D and E, which contained nearly the same proportion through 200-mesh, show also that as the total amount of through 50-mesh dust is decreased the inflammability decreases.
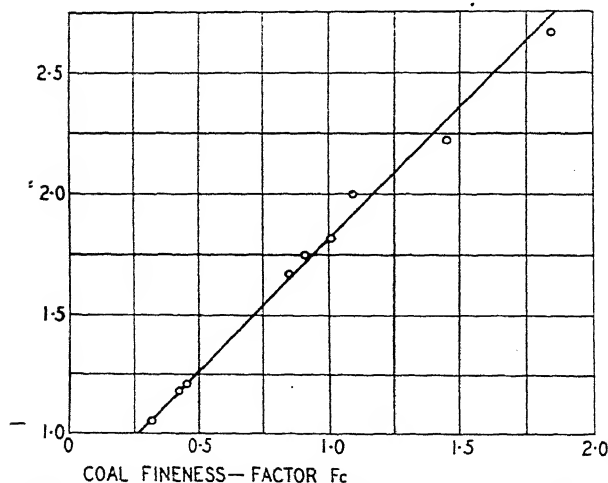
FIG. 4.—Relationship between fineness and inflammability.

the Fineness of the Dust Preparation. — It can be assumed that the specific surface of a dust particle is inversely proportional to its mean diameter, and that the average mean diameter of the particles in a sieved fraction is the mean of the widths of the two meshes between which the fraction lies. A proportional factor can then be assigned to each sieved fraction of a dust preparation, except that which passes through the finest sieve.   To that fraction an arbitrary factor must be assigned.   This method has been used to assess the relative fineness of the preparations used for the tests of

inflammability. The factors used for each sieved fraction are recorded in Table III.

With these factors for each sieved fraction, together with an arbitrary value 2·000 for the fraction passing through a 200-mesh, the composite fineness factor, F_c, for each of the dust preparations has been calculated from its sieving analysis, as shown in Table IV.

TABLE IV.—THE FINENESS FACTORS (F_c) OF THE COAL DUST PREPARATIONS.

Prepara-tion.	3-5 (0·0028).	5-8 (0·046).	8-20 (0·086).	20-50 (0·214).	50-100 (0·500).	100-200 (1·000).	Through 200 (2000).	Fineness Factor F_c.
A.	—	—	—	—	0·005	0·14	1·70	1·85
B.	0·001	0·003	0·005	0·009	0·010	0·13	1·30	1·46
C.	—	—	0·003	0·034	0·115	0·22	0·72	1·09
D.	—	—	0·003	0·071	0·065	0·14	0·72	1·00
E.	0·002	0·008	0·011	0·021	0·020	0·10	0·76	0·92
F.	—	—	0·025	0·045	0·035	0·11	0·64	0·86
G.	—	—	0·034	0·062	0·055	0·09	0·22	0·46
H.	0·002	0·010	0·021	0·041	0·040	0·07	0·24	0·42
J.	0·003	0·013	0·020	0·034	0·030	0·06	0·16	0·32

In Fig. 4 the factors F_c for the preparations are plotted against their inflammability indices, $100/(100 − S)$. The graph shows a linear relationship which can be expressed by the formula : $100/(100−S) = 1·1 \ F_c + 0·7$, whence $S = 100 − 100/(1·1 \ F_c + 0·7)$.

Any deviation from the relationship expressed by this formula is within the limits of experimental error of 2·5 per cent. stone dust for the determination of inflammability.

THE SPREAD OF SMOKE AND GASES FROM CHIMNEYS.

By C. H. BOSANQUET, M.A., AND J. L. PEARSON, B.A., PH.D.

I. Introduction.

The authors have dealt elsewhere[1] with the following theoretical and practical aspects of the spread of chimney emissions :—

(a) a physico mathematical analysis of the phenomena involved in eddy diffusion ;

(b) space-concentration distribution and mass-over-area distribution of emission from point and from line sources ;

(c) the effects of chimney height on space-concentration and mass-over-area distributions.

Mass-over-area distribution of atmospheric pollution from chimney emissions is of practical importance, since it determines :—

(a) in rainy weather, the amount of acid and dust brought down by the rain,

(b) in fine weather, the extent of the curtailment of sunshine and ultra-violet rays.

[1] *J. Inst. Elec. Eng.,* July, 1935, and *J. Inst. Fuel,* April, 1935.

Space-concentration distribution governs the general environment of pollution, to which buildings and people are subjected when it is not raining, the effects from acids being dependent on and those from dust being largely independent of humidity. In a sense, ground level concentrations should not be of great practical importance, since, in any civilised community, they are presumably already maintained below the extent to which they become actively inimical to health or injurious to vegetation.

In this paper the mathematical analysis of the phenomena involved in eddy diffusion is carried further, with results that indicate that :—

    (a) any reasonable theoretical treatment of the subject-matter, utilising any reasonable assumptions, leads to closely identical conclusions carrying similar practical implications ;

    (b) the earlier and more general treatment of the subject, as mentioned above, presents a fairly correct picture of the mechanism and effects of eddy diffusion, and is reasonably consistent with ascertained facts and experimental data.

This paper, however, presents a more acceptable theory concerning vertical diffusion.

It should be noted that, in practice, no theoretical assumptions at all have to be made in order to determine :—

    (a) the mass-over-area distributions from continuous emission by point or line sources, as averaged over long intervals of time, say a year;

    (b) similar distributions over short intervals of time when the wind is swinging, to and fro, through an angle of the same order as that of the cone of discharge.

With regard to distant ground concentrations arising from sources of continuous emission and as averaged either over long periods of time or over shorter periods with average wind swing, the only assumption is that concerning the effects of vertical diffusion. Up to distances of, say, fifteen chimney heights from the source, there can be little doubt about the ground concentrations, owing to the emission taking a form which is so often visible.

The authors wish to call attention, in particular, to the widespread misconceptions that have existed in the past concerning :—

    i. chimney height: It can now be clearly shown that any increase above a reasonable height has no practical effect.[2]

    ii. concentration at moment of emission : This is really of very little importance indeed in practice, the most important factor in the problem of atmospheric pollution being the mass rate of emission of the objectionable constituents for any and every particular case.

II. The General Case of Eddy Diffusion (i.e. for a single Dispersing Cloud).

In a wind gases and dust will be dispersed more rapidly than in still air, since eddy diffusion arising from the effects of turbulence in the dispersing medium will be superimposed on the effects of kinetic diffusion and Brownian motion. Eddy diffusion coefficients found in practice vary considerably, but, in all cases, they are very large compared to the ordinary coefficients of the kinetic theory. The effects of these latter can be neglected in comparison.

In eddy diffusion the variations of velocity from place to place correspond to velocities of agitation, and the average distance an

[2] For a suggested criterion of reasonable height see *J. Inst. Elec. Eng.*, July, 1935.

individual portion of gas moves before losing its sense of direction corresponds to the free path.

G. I. Taylor [3] has shown that there is no need to postulate anything definite about the type of motion of individual portions of gas in order to investigate the spreading of such properties as composition and momentum. All that is necessary is to assume that the correlations at different times between the vector velocities and the properties of the portion of the gas are functions of the time difference, the correlation decreasing from unity to zero with increasing time difference. The following analysis differs considerably from his, but is based on the same fundamental ideas.

Consider a gas in which a property C varies along the x axis. Let the root-mean-square velocity fluctuations of individual portions of gas be u. Let v be the velocity component along the x axis, and let $F(t)$ be the correlation between the values of v of the same portion of gas at times differing by t. Also, if the value of C varies from one portion of gas to another, let the correlation between the deviations of C from the mean of the surroundings at times separated by t be $f(t)$. If $f(t)$ is independent of the deviation from the mean, then the probable deviation will decrease by equal percentages in equal time, so that

$$f(t) = $$

Consider the case of a portion of gas whose velocity component along the x axis at the zero of time is v. At time $- t$ let it be in a region where the mean value of C is C_t, then when $t = 0$ the probable value of C of the portion considered is given by :—

$$_0 \qquad \qquad \qquad \qquad \qquad (1)$$

At time $- t$ the probable value of dx/dt is equal to $vF(t)$, so that the probable value of x is :—

$$x_0 - v \int_0$$

and the probable value of C_t is therefore :—

$$\qquad \qquad \qquad \qquad (2)$$

Combining equations 1 and 2, the probable value of C can be found as a function of v. If, for instance, $F(t) = e^{-L(t)}$ then the probable value of C will be :—

This leads to a diffusion coefficient

Any assumptions as to the form of $f(t)$ and $F(t)$ will yield an expression of this type. D is proportional to u^2 divided by the sum of two terms, K a rate of mixing term, and L a rate of loss of momentum term. K is obviously proportional to D and L is proportional to the effective kinematic viscosity of the gas. Now the kinematic viscosity is the diffusion

[3] *Proc. Lond. Math. Soc.*, 1922, **20**, 196.]

coefficient of the special property momentum and in eddy motion the diffusion coefficients of all properties will be equal, so that L is also proportional to D.

By any theory the rates of mixing of similar portions of gas with their surroundings will vary directly as the diffusion coefficient and inversely as the square of their linear dimensions. If $\phi(r)$ is the correlation coefficient between simultaneous values of v at points separated by a distance r, then the effective radii of the individual portions of gas will be proportional to :—

$$\int_0^\infty \phi(r)\mathrm{d}r.$$

Then

$$D \propto \frac{u^2\left(\int_0^\infty \phi(r)\mathrm{d}r\right)^2}{D}.$$

Therefore

$$D \propto u\int_0^\infty \phi(r)\mathrm{d}r \qquad . \qquad . \qquad . \qquad . \quad (5)$$

$\int_0^\infty \phi(r)\mathrm{d}r$ is of the dimensions of a length, and can be roughly described as being the mean radius of an eddy. In the case of a smoke cloud from a chimney, the billows in its outline will be separated by a distance of the order of four times this length.

If the flow pattern in a wind is independent of the wind velocity, then u must be proportional to the wind velocity. This seems to be borne out in practice, since it is generally agreed that the eddy diffusion coefficient is proportional to the wind velocity, i.e. the spreading of a cloud depends on the distance it has drifted down wind, and not on the time taken over the distance.

The phenomena of eddy diffusion will differ in three important respects from gas kinetic diffusion, viz. :—

i. all gases as well as suspended particles will diffuse at the same rate, and the diffusion coefficient will probably be numerically equal to the kinematic eddy viscosity and to the thermal diffusivity ;

ii. the diffusion coefficient will increase with wind velocity, probably being nearly proportional to it ;

iii. the diffusion coefficient will tend to increase as the scale of the phenomena increases.

This latter conclusion, already stated by Sutton,[4] can be obtained in various ways. In considering the spreading of a cloud, it is obvious that only velocity fluctuations within the cloud can be effective in causing dispersal of the cloud, so that in equation 5 the value of u is the root-mean-square of the velocities of points in the cloud relative to the centre of gravity of the cloud. It is obvious that greater velocity fluctuations will occur in a cubic kilometre of air than in a cubic centi-metre, so that u will tend to increase with the size of the cloud. The mean difference of the velocities at two points separated by a constant distance r will, however, be a function of r only so that the correlation between the velocities at two points fixed relative to each other will

[4] *Proc. Roy. Soc.*, 1932, **135**, 143.

tend to increase as u increases. Hence, both u and $\int_0^\infty \phi(r)\,dr$ increase with the size of the cloud.

The problem can also be dealt with by dimensional analysis. The diffusion coefficient can be assumed to depend only on :—

the wind velocity .	.	.	.	.	.	v
the kinematic viscosity	.	.	.	.	.	ν
some undefined length .	.	.	.	.	.	l

The kinematic viscosity here is the ordinary kinematic viscosity, not the kinematic eddy viscosity. l may be the height above ground, the mean radius of the cloud, the distance the cloud has drifted from its source, or some kind of weighted mean of all three. In any case, the relation must hold that

$$D = vl\,f\!\left(\frac{vl}{\nu}\right) \quad .$$

If $D \propto v$, as suggested above, then $f\!\left(\dfrac{vl}{\nu}\right)$ must be a constant, it is also a matter of common experience in hydraulics and aero-dynamics that large scale phenomena are uninfluenced by viscosity, leading to the same conclusion.

It can therefore be assumed that D is very nearly proportional to vl for phenomena on a meteorological scale.

If the standard deviation σ be defined as the root-mean-square of the displacements of the constituents of a cloud from a plane passing through the centre of gravity and normal to the direction in which diffusion is being considered, then by the ordinary laws of diffusion

$$\frac{}{dt} = \frac{}{\sigma}.$$

If a cloud has its origin at ground level, and cross-sections of the cloud after drifting different distances downwind are similar then $\bar{z}$, the mean height above ground, is proportional to σ. If, therefore, l can be identified with σ or $\bar{z}$, and if $D \propto v$, it can be seen that $d\sigma/dx$ is constant where x is the distance the cloud has drifted from the source. Thus x, $\bar{z}$ and σ are all proportional to each other, and it makes no difference except to the numerical constant which of them is identified with l.

This analysis leads to the conclusion that $\sigma \propto x$. Now, the cross-section of a cloud from a continuous point source such as a chimney is proportional to σ^2, so that the mean density in such a cloud varies as the inverse square of the distance from the source. It is shown by Sutton [4] that an inverse square law of decrease of density is a limiting case corresponding to perfect correlation between the motions of a portion of air at all times. He gives evidence, however, to show that the law is very closely approached in practice, so that variations of the turbulence of the air with weather conditions and with the nature of the ground will probably cause far greater errors in calculated values of the mean cross-section of a cloud at various distances than will a small deviation of n from unity in the formula $D \propto \sigma^n$.

III. Diffusion of a Gas Constituent from a Continuous Line Source.

A. In deriving a formula for the concentration of flue gas in the atmosphere at different points downwind from a chimney, it is convenient to treat the horizontal and vertical diffusions separately. The two diffusions will follow rather different laws owing to the effect of the ground, so that vertical diffusion takes place in a semi-infinite space instead of an infinite space.

Consider first a continuous line source of atmospheric pollution such as a row of chimneys, which is long compared to σ.

It can be seen by watching a persistent smoke cloud coming from a chimney that, at points a few chimney heights away downwind, the cloud sometimes appears to be in contact with, and sometimes rises clear of the ground. It is necessary, therefore, to consider either the maximum instantaneous pollution density at a point or else the average over a time long compared with the time of passage of an eddy. This long time average will be considered here.

In this case it is necessary to take account of vertical movements of the centre of gravity of the cloud as well as of the spreading of the cloud, since the average concentration at any point is equal to the product of the average concentration when the cloud overlaps the point and the fraction of the total time during which overlap occurs. For a cloud whose sinuosities are large compared to its diameter, the average concentration inside the cloud varies inversely as the square of the diameter and the time varies almost directly as the square of the diameter, so that the time average depends almost entirely on the amplitude of the sinuosities, and is nearly independent of the actual diameter of the cloud. The diffusion coefficient in the vertical direction then depends only on the root-mean-square of the vertical component of the wind velocity and on $\phi(r)$. These are both independent of the presence or absence of the cloud, so that D must be independent of both x and σ, and l must therefore be identified with z, the height of the point above ground.

The diffusion equation can therefore be written

$$D = pzv \qquad . \qquad . \qquad . \qquad . \qquad (7)$$

where p is a numerical constant.

If diffusion can be neglected in the horizontal plane, i.e. if the source is a line source giving no cross wind variation of C, and if the concentration gradient in the direction of the wind is small compared to the vertical concentration gradient, then :—

$$\frac{dC}{dx} = p\frac{d}{dz}\left(z\frac{dC}{dz}\right) \qquad (8)$$

It appears an extraordinary conclusion at first sight that the diffusion coefficient should be least near the ground where the turbulence is expected to be greatest; however, the effect of the ground is to reduce the correlation between values of velocities at neighbouring points, i.e. to reduce $\int_0^\infty \phi(r)dr$. Further, components of velocity normal to a surface must vanish at that surface.

B. Derivation of a Formula for Concentration at Ground Level due to a Line Source at Finite Height.

If a line source situated at a height h above ground emits a mass M of some constituent per unit length in unit time, then if the wind velocity is v at all points

$$\int_0^\infty C dz = \frac{M}{v} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (9)$$

Combining equations 8 and 9, a complete solution can be obtained for the special case $h = 0$ in this case ;

$$C = \frac{M}{pvx} e^{-\frac{z}{px}} . \qquad . \qquad . \qquad . \qquad . \qquad (10)$$

In the general case, it is possible to analyse the distribution in the plane $x = 0$ into a series of exponentials similar to a Fourier series, so that the combined effect of a number of positive and negative line sources at ground level, at points upwind of the actual source, will combine to produce a line source of strength M at height h in the plane $x = 0$.

If the virtual sources are of strengths A, B, C, etc., situated at $x = -d$, $x = -d/2$, $x = -d/3$, etc., then the conditions to be satisfied are :—

$$A + B + C + \ldots = M$$

$$C = \frac{1}{pvd}\Big(A e^{-\frac{z}{pd}} \qquad^{2z}$$

when z is unequal to h.

These conditions are satisfied if $\frac{pd}{h}$ is vanishingly small and

$$A = M e^{\frac{h}{pd}}$$

$$B = -\frac{M}{2!}e$$

$$\frac{M}{3!}\quad^{3h}$$

Then

$$C = \frac{M}{pvd}e^{\psi - e^r}.$$

This expression is obviously vanishingly small for moderately large positive or negative values of ψ, and as d is decreased indefinitely, the distribution approaches more and more closely to a line source at height h.

For positive values of x :—

$$\frac{}{pvx}\left\{ e^{\frac{1}{p}\left(\frac{h}{d} - \frac{z}{x+d}\right)} \quad e^{\frac{2}{p}\left(\frac{h}{d} - \frac{z}{2x+d}\right)} \quad e^{\frac{3}{p}\left(\frac{h}{d} - \frac{z}{3x+d}\right)} \right.$$

The only place where the value of C is important is ground level, so that the special case of $z = 0$ will be considered.

Then $\qquad\qquad\qquad \dfrac{h}{p \log u}.$

Substituting this value in equation 11, and expanding the series in powers of u and $\dfrac{d}{x}$ gives :—

$$= \frac{M}{pvx}\left\{\left(u - \frac{u^2}{2!} + \frac{u^3}{3!} - \ldots\right) - \frac{h}{px \log u}\left(u - \frac{u^2}{2\,.\,2!} + \frac{u^3}{3\,.\,3!} - \ldots\right)\right.$$

C is given by the limit of the sums of these series when u tends to infinity.

The sum of the first series is obviously $1 - e^{-u}$, and if each series be divided by u and then integrated with respect to u the result is the succeeding series.

The sums of the series for large values of u are therefore equal to :—

$$1, \quad \log u + K, \quad \frac{\log^2 u}{2!} + K \log u + L, \text{ etc.}$$

Where K, L, etc., are numerical constants.

$$\therefore \quad C_0 = \frac{M}{pvx}e^{-\frac{h}{px}}$$

$$pvx^- \qquad\qquad . \tag{12}$$

since d is vanishingly small.

C_0 is a maximum when $x = \dfrac{h}{p}$, and when x is large compared to $\dfrac{h}{p}$, the exponential term becomes unity, and C falls off inversely as the distance.

C. The General Case where $D = pvz^n$.

Comparison of equations 10 and 12 shows that the value of C at ground level due to a source at height h is the same as the value at height h due to a source at ground level. This is also obviously true for a diffusion coefficient independent of height, and may be assumed to be generally true for any law of diffusion.

The general equation :—

$$\frac{dC}{\qquad} \quad \frac{d}{\qquad}\left(\frac{dC}{\qquad}\right)$$

can be solved for a source at ground level, so that if the above theorem be used

$$C_0 = \quad 2-n \qquad M \qquad \frac{h^{2-n}}{\qquad} \qquad . \tag{13}$$

The maximum value of C occurs when $px = (2-n)h^{2-n}$, and the maximum concentration varies between $0\cdot 48\dfrac{M}{vh}$ for $n = 0$ and $0\cdot 37\dfrac{M}{vh}$ for $n = 1$.

The value of the concentration at the maximum is thus seen to be almost independent of the law of variation of diffusion with height and quite independent of the value of the turbulence constant p.

IV. Diffusion of Dust from a Continuous Line Source.

Equation 12 is derived on the assumption that no matter is lost from the cloud, and that gravity is without effect. In the case of dust particles, a steady fall must be superimposed on the dispersion, and all particles which strike the ground will be assumed to be retained. The result of this will be that the total mass of the cloud will decrease with distance.

Again, consider the case of an infinite line source of strength M, and let the free falling speed of the particles be equal to f.

The diffusion equation now becomes :—

$$(14)$$

and

$$\frac{\mathrm{d}}{\mathrm{d}x}\int_0^\infty C\mathrm{d}z = -C_0\frac{f}{v}. \qquad . \qquad . \qquad . \qquad (15)$$

Equation 14 is equation 8 with a term added to allow for the fall of the particles, and equation 15 gives the rate of loss of mass from the cloud due to the settling out of the particles.

If the source is so distant that the effect of height of emission is negligible, the solution of these equations is :—

$$\frac{A}{x^{1+\frac{f}{pv}}}e^{-\frac{z}{px}} \qquad . \qquad . \qquad . \qquad . \qquad (16)$$

In the case of a gas $f = 0$, and for a very distant source C and C_0 are expressed by equations 10 and 12 respectively for a source at height h at any distance. The formula for the case of dust must be of the same type as that for a diffusing gas, since the latter is a limiting case of the former. At small distances from the source, the falling of the dust will tend to increase the ground concentration, and at great distances the reduction of total mass of the cloud will cause it to fall below that given by the gas formula.

If the ground concentration is independent of f at a distance X, then a possible form of the formula is

$$C_0 = \frac{MX^{\frac{f}{pv}}}{pvx^{1+\frac{f}{pv}}}e^{-\frac{h}{px}} \qquad (17)$$

Since all the dust will eventually settle, and the amount settling on unit area in unit time is equal to $C_0 f$, we have the relation

If f/pv is small, this condition is satisfied by equation 17 if $X = 1\cdot78\dfrac{h}{p}$.

then

$$\frac{h\backslash f}{pvx^{1+\frac{f}{pv}}}e^{-\frac{\cdots}{px}}. \qquad . \qquad . \qquad . \qquad (18)$$

No formal proof of this formula has been obtained, but it is of the right form and gives the correct values for large values of x, and small values of f/pv. An additional check can be obtained by evaluating

$$\int_0^\infty C_0 \mathrm{d}h = M/v.$$

This gives the value of C_0 due to an infinite vertical plane source emitting a mass M per unit area per unit time. At all points downwind of such a source, the value of C must be M/v, since no concentration gradients are present, and consequently there is no diffusion. This gives additional confirmation to equation 18. At great distances, then, the ground level concentration of dust from an infinite line source at any height above ground will fall off rather more rapidly than the inverse first power of the distance, the falling off being more rapid the larger the particles.

V. Diffusion from a Continuous Point Source.

If the source is concentrated at a point such as the top of a chimney, instead of being spread over an infinite line across wind, the lateral spreading must also be taken into account.

Here the duration of the sample time is of even more importance than in the case of vertical diffusion from a line source. If a really long sampling period be required, e.g. if it is desired to estimate the average atmospheric pollution during the whole year, then the governing factor will be the distribution of direction of the wind. The instantaneous width of the smoke cloud will be without effect in this case, since increase of width will decrease the average concentration in the cloud and increase the frequency with which the cloud overlaps any given point, the two effects exactly cancelling each other.

If the fraction of the year during which the wind direction falls within an arc θ be $a\theta$, and the mean wind velocity be v, then the average value of C for the whole year due to a chimney emitting a mass M of gas per unit time will be

$$\frac{Ma}{pvx^2}e^{-\frac{h}{px}} \qquad . \qquad . \qquad . \qquad . \qquad . \quad (19)$$

The mean value of a will obviously be $\frac{1}{2\pi}$, and the variation of a with direction can be obtained from meteorological records, and is independent of any diffusion theory.

Equation 19 gives the value of C which is effective in all cumulative processes, such as the blackening of the neighbourhood by soot, and to a great extent the attack of structures by acid constituents of flue gas such as oxides of sulphur and nitrogen and HCl.

At points not far distant from a chimney, effects due to the maximum concentration over short periods may become of importance, e.g. the gases may be smelt, and in this case the effective sampling period can be taken as of the order of a few minutes to an hour, i.e. a period during which the mean wind direction is not likely to change appreciably.

In this case, at points which are situated at a distance from the chimney smaller than the velocity of the wind multiplied by the mean duration of the minor transitory changes of direction, the lateral spreading of the mean cloud will be governed by the swing of the wind and equation 19 will hold with a suitable value of a.

If σ be the standard deviation referred to a vertical plane through the mean axis of the cloud, then

$$\sigma \propto x.$$

Now

$$\frac{d\sigma}{dt} = \frac{D}{\sigma}.$$

$$\therefore \quad \frac{d\sigma}{dx} = \frac{D}{v\sigma}.$$

If, therefore, $\sigma \propto x$, then $D \propto \sigma v \propto vx$. At distances such that σ is great compared to h, $\bar{z} \propto x$ and, as pointed out above, in these circumstances in the formula $D \propto vl$, it makes no difference whether l be identified with σ or $\bar{z}$. Again, therefore, at great distances $D \propto \sigma v$, so that σ/x is constant.

In the case of gas emission, the total mass of unit length of the cloud will be everywhere equal to M/v. The mass m over unit area of the earth's surface at a distance x downwind, and y to one side of the mean path of the cloud, must be a maximum when $y = 0$, and fall off to zero at values of y large compared to σ. If the diffusion coefficient be assumed to be a function of x or σ only, and independent of y, and if concentration gradients along the cloud be assumed small compared to those at right angles to its mean direction of motion, then

$$\frac{\partial m}{\partial x} = \frac{D}{v} \cdot \frac{\partial^2}{\partial y^2}.$$

These conditions are satisfied by the equation

$$m = \frac{M}{\sqrt{2\pi}\,\sigma v}e^{-\frac{y^2}{2\sigma^2}} \quad . \qquad . \qquad . \qquad . \qquad . \quad (20)$$

If $D = qv\sigma$ then $\sigma = qx$.

$$m = \frac{M}{\sqrt{2\pi}\,qxv}e^{-\frac{y^2}{2q^2x^2}}. \qquad . \qquad . \qquad . \qquad . \quad (21)$$

Substituting this value of m for M in equation 12 gives for the ground level concentration due to a continuous point source,

$$\frac{M}{} \qquad -\frac{h}{} - \frac{y^2}{} \qquad\qquad (22)$$

Similarly, for the case of dust with a free falling speed of f,

$$. \qquad . \qquad . \quad (23)$$

$$\sqrt{2\pi}pqx \qquad pv$$

VI. Comparison with Experiment and Numerical Values of p and q.

The value of p can be estimated in various ways. Hellmann,[5] from experiments over an open field at heights of from 2 to 32 metres, found that the wind velocity varied approximately as $z^{1/5}$. This is in general agreement with the observation that the velocity of a gas flowing in a

[5] *Met. Z.*, 1915.

pipe varies in the region of the pipe wall proportionally to the $1/7$ power of the distance from the wall. A later formula of Hellmann gives

$$v = a \log (z + b) - c,$$

where a, b and c are constants.

The mean of Hellmann's first formula and the pipe results gives $\frac{dv}{dz} \propto z^{-5/6}$, and Hellmann's second formula gives $\frac{dv}{dz} = \frac{a}{z+b}$. Now the product of the velocity gradient and the effective eddy viscosity must be constant and equal to the tangential force per unit area on the ground. Since the diffusion coefficient can be identified with the kinematic eddy viscosity, these two formulæ indicate that $D \times z^{5/6}$ and $D \propto z + b$ respectively, agreeing reasonably well with the assumption made in this paper that $D \propto z$. An approximate estimate of p can be made from the first formula. It is known that above about 500 metres the wind velocity agrees well with the value calculated from the horizontal baro-metric pressure gradient. Also the tangential force per unit area on a plane for large scale phenomena tends to the limiting value of about $0.002 \, \rho V^2$, where V is the velocity at points remote from the plane. If then the velocity be assumed to vary as $z^{1/6}$ up to 500 metres, after which it becomes constant, then

$$\frac{dv}{dz} = \frac{V}{6(5 \times 10^4)^{1/6}} z^{-5/6},$$

and

$$0.002 \, \rho V^2 = \rho D \frac{dv}{dz},$$

$$\therefore D = 0.073 \, VZ^{5/6}.$$

If v be the velocity of the wind at 100 metres, then the value of D at 100 metres is $0.02 \, vz$. This gives $p = 0.02$, a value which is probably too low, since the tangential force of $0.002 \, p\bar{V}^2$ was obtained by experi-ments with smooth pipes and the tangential force on the earth's surface may well be considerably greater. If a cloud from a chimney be viewed from the side, then the opacity is probably a function of the total amount of matter in the line of sight. The apparent density will be equivalent to that from a line source, since lateral spreading is without effect on the opacity. The apparent greatest density at ground level then will occur when $px = h$, or at a distance $1/p$ chimney heights from the source.

Dobson,[6] in a memorandum on atmospheric turbulence, gives a composite of eight successive photographs of a smoke cloud from a chimney. The maximum density at ground level is apparently about seven chimney heights from the source, giving $p = 0.14$. He states that on another day the apparent turbulence was 0.4 times as great, giving $p = 0.06$. In this case, there were a number of buildings immediately to leeward of the chimney, so that more turbulence would be expected than in Hellmann's case.

Experiments by Richardson[7] on smoke clouds from small sources near the ground give a mean standard deviation in the vertical direction of 0.45 m. at a distance of 5 m. from a source 2 m. above ground. This leads to a value of p of 0.01, but these experiments again were carried out over a smooth field where the turbulence would be expected to be low.

[6] Advisory Committee for Aeronautics, Reports and Memoranda No. 671, 1919.

[7] Phil. Trans., 1920, 221A, 1.

An average value of p is probably about 0·05, with possible variations by a factor of at least 3 in either direction. This value would make the apparent greatest density at ground level of the smoke cloud from a chimney occur at a distance of twenty chimney heights, whilst the actual maximum density, allowing for lateral diffusion, would occur at half this distance.

B. The Value of q.

Experiments by Richardson and Porter [8] on the horizontal scatter of small balloons released nearly simultaneously and drifting distances of between 30 and 600 km. give a mean value of σ in the horizontal direction of 16 km. at a distance of 200 km. the best fit to their points being obtained if $\sigma \propto x^{0·9}$. This gives a mean value of q of 0·08 over this range of distances.

Now, the value of σ for horizontal diffusion is qx; but for vertical diffusion from a source at ground level if $D = pzv$, then $\sigma = \sqrt{2}\,px$. If, therefore, σ is the same in the horizontal and vertical directions, and the cross-section of a smoke cloud is roughly circular or semi-circular, according to whether it is formed at a great height or near the ground, then $q = \sqrt{2}p$. This indicates a value of p of 0·057 from the balloon results, in agreement with the mean value at short distances.

C. Sootfall in and near Towns.

It has been deduced above that the rate of deposition of dust at a distance x from a line source of intensity M is equal to

$$\frac{Mf}{x^{1 + \frac{f}{pv}}} \left(1·7\xi \right.$$

where h is the height of the source above ground.

The D.S.I.R. Report on Atmospheric Pollution for 1931 gives an account of experiments which were carried out in the neighbourhood of Norwich. Norwich can be considered in this case as a line source of smoke about 2 miles in length. At distances between 2 and 10 miles from the centre of the city the rate of dust deposition at points immediately downwind varied as $A + B/x$, A being the rate of deposition of non-city dust. This agrees with the formula above if f/pv and h/px are both small. The value of f for a 20 micron diameter coal particle in air is 1·5 cm./sec., the mean value of v is about 500 cm./sec., and p can be taken as 0·05.

For particles of this size, $f/pv = 0·06$. The mean height of the chimneys of Norwich is probably about 15 metres, so that at a distance of 2 miles from the centre of the city, $e^{-h/px}$ will vary between 0·83 and 0·94. This difference from unity is partially compensated by the effect of the finite depth of the city, the mean value of $1/x$ being $\frac{1}{2}\log_e 3 = 0·55$, instead of 0·50 at a distance of 2 miles from the centre of the city. It would be expected, therefore, that the inverse first power law would hold with reasonable accuracy, as was found in practice.

It will be noticed that although there is a considerable range of values of p deducible from different sets of experiments, yet there is no apparent tendency for p to decrease as the scale of the experiments is

increased ; in fact, the smallest values are deduced from the smallest scale experiments (Richardson). If n is appreciably less than unity in the expression $D = pvz^n$, then the value of p deduced on the assumption that $n = 1$ should fall off with distance from the source according to the

law $px^{2-n} = const.$

This confirms the statement made above that effects due to the deviation of n from unity are unimportant compared to the variations of p with conditions of weather and surface.

VII. General Conclusions and Applications.

A theory has been developed by dimensional analysis for calculating the spreading of a smoke cloud from a chimney, and the results have been
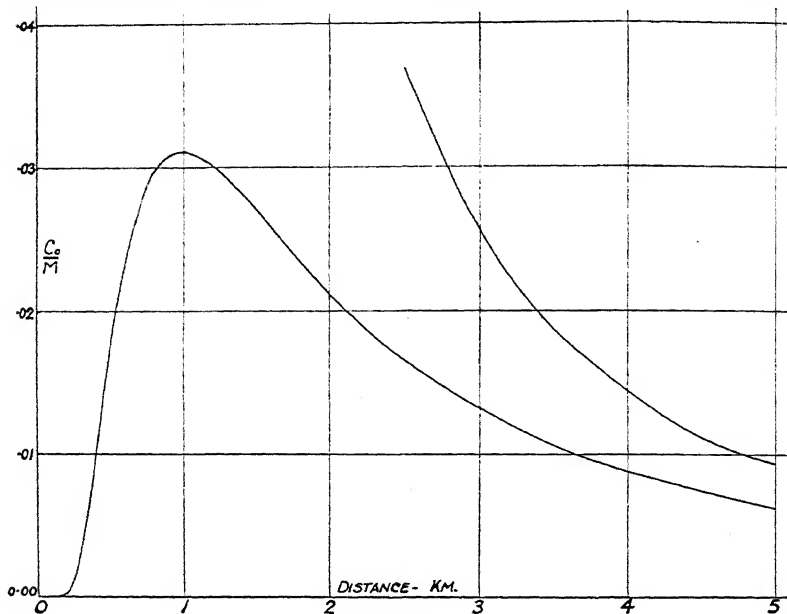
FIG. 1.

shown to agree reasonably well with experiment. At points close to the chimney the concentration at ground level is small, since but little smoke has diffused down to the ground. At a distance of the order of ten times the height of the chimney the smoke concentration at ground level reaches a maximum. The concentration at that maximum varies inversely as the square of the chimney height, and its actual value is almost independent of assumptions as to the variation of diffusion coefficient with height. At greater distances the concentration at ground level falls off again until after about fifty chimney heights the concentration varies as the inverse square of the distance and is independent of chimney height.

A formula is given for the concentration at all distances from the chimney foot.

Assuming that $p = 0.05$ and $q = 0.08$ ·

$$C \qquad \frac{100\,M}{} \, {}_{-}\frac{20h}{} \, {}_{-}\frac{78y^2}{}$$

The figure gives values of $\dfrac{C_0}{M}$ for various values of x for a chimney one hundred metres high, with a wind velocity of 5 m./sec. C_0 is in milligrammes per cubic metre, M is in metric tonnes per day, and the values are those for $y = 0$, *i.e.* at points on the ground directly under the axis of the cloud. The upper curve gives values of C_0 if $h = 0$, *i.e.* the difference between the two shows the effect of chimney height in reducing the atmospheric pollution at ground level. With a chimney 100 metres high the concentration is halved at 2·9 km., and at greater distances the effect of chimney height becomes progressively smaller. Over the range of distances covered by the curve the variation of dust concentration with distance is indistinguishable from that for gases, since the curves intersect at 3·56 km, and the slopes are very nearly the same for particles of the order of 20 microns diameter. This is not surprising, since in the absence of diffusion, coal particles 20 microns in diameter would not reach ground until they had drifted 33 km.

It may be pointed out that the general form of the curves is independent of any theory as to the variation of diffusion with height. In particular, the ratio of the yearly average contaminations produced by different types of source such as a power station and a town, at distances great compared to the chimney heights are independent of all theory. This point is stressed because this investigation was originally begun in order to find whether the superposition of the products of combustion of a power station in a town on those of domestic fires would cause an appreciable increase and in order to estimate the improvement attainable by using tall chimneys.

It is seen that although the improvement is great in the immediate locality, yet a mile or two away the effect of chimney height disappears completely.

GENERAL DISCUSSION.

Mr. F. I. G. Rawlins (*London*) said : It would be of great use to those who have to consider the influence of fogs and dust upon buildings and their contents if they could be provided with a three-dimensional scheme showing, not only the amount of material deposited at ground level at given distances from a chimney, but also the vertical distribution. Clearly, local conditions would influence the relationships enormously, but any method of obtaining a rough idea of the amount of deposit to be expected on the roof of a building of given height at a given distance from a chimney would be of considerable practical value. One imagines that fog and dust " shadows " are presumably cast by large obstacles, and this could be allowed for if some indication of vertical distribution could be obtained as a function of the other two variables.

Mr. G. Nonhebel (*Billingham*) said : It has been shown from the principles of eddy diffusion that the maximum ground concentration occurs at a distance of the order of ten chimney heights from the base of the chimney. A curve for one particular set of circumstances is given by Pearson and Bosanquet in Section VII. of their paper. For other circumstances, the maximum ground concentration C_0 in mgs./M³ at the centre of the line of discharge will be roughly

$$C_0 = \frac{1 \cdot 55 \times 10^3 M}{v h^2},$$

where M = mass rate of emission in tons/day, v = wind velocity in m./sec. h = chimney height in m. From this it may be deduced that when the wind -velocity is relatively low at 2 m./sec. and the emission is 60 tons SO₂/day, the maximum ground concentration with a chimney height of 330 ft. (100 m.) is 5 mgs. SO₂/M³. (A diagram showing the progressive

increase in chimney height required to keep the ground concentration below 5 mgs./M³ has been recently published.) [1]   This is not an unreasonable factor of safety, and yet few of the larger power stations fulfil this condition.

It is evident that further experimental observations are urgently required on diffusion of smoke from chimneys, and biological experiments on the toxic effects of SO_2 and SO_3 are similarly required.   It would be of interest, also, to know how much of the SO_2 in an atmosphere is oxidised to SO_3 when it is dissolved in the moisture in the lungs.

Mr. C. H. Bosanquet (*Billingham*) said in reply : Measurements of numbers and size distributions of particles in the air at different distances from the source would be of great use in testing the theory.   The size distribution should only vary very slowly with distance for particles less than 20μ in diameter.

In reply to Rawlins : Small particles in the air will diffuse as a gas so that no true shadows can be produced by buildings.   If a building is close enough to the source for an appreciable vertical concentration gradient to exist, then the downward currents behind the building are more likely to produce an increase than a decrease of concentration.   Large particles will certainly be deposited preferentially on the windward face of a building, but diffusion close to the lee side will be abnormal due to the local disturbance of flow.

[1] Pearson, Nonhebel and Ulander, *J. Inst. Elec. Eng.*, 1935, **77**, 1.

THE DISSIPATION OF FOG.

BY PROFESSOR D. BRUNT, M.A.

1. The Formation of Fog.

Fog is formed in air which is initially clear but damp, when the air is cooled to a temperature below its dew-point.   The temperature of the air immediately above the surface of the earth is controlled by the temperature of the surface.   The cooling necessary for the formation of fog may be produced in two ways ; (*a*) by the loss of heat by long-wave radiation from the ground at night to a clear sky, or, (*b*) by the motion of warm damp air into a region where the surface of the earth is cold. Fogs formed by method (*a*) are known as " radiation fogs." Their formation requires a clear sky, and very light wind or calm.   They do not form to the same extent on windy nights, as the turbulent mixing associated with strong winds distributes the loss of heat through so deep a layer that the dew-point is not attained.

Fogs of type (*b*) may form either over land or sea.   At sea they form in such regions as the Great Banks of Newfoundland, where a warm damp current of air from the Gulf of Mexico flows over a sea surface cooled by the Labrador Current.   Fogs form in precisely the same way over land, when, after a spell of cold weather during which the ground has become cold, a warm damp south-westerly current sets in.   Such fogs may persist for days, with visibility limited to less than 100 metres. An example of such a fog occurred on Saturday, 15th February, 1936, persisting in places until the early morning of the 17th.   After a week of fair and rather cold weather, a warm damp south-westerly current of air set in during the night of the 14th-15th.

2. Some Physical Facts.

Dense radiation fogs usually extend through a depth of 300 to 800 feet, while the temperature increases upward from the ground to the top of the fog by an amount which averages about 5° C. The amount of liquid water in a fog is from 3 to 8 per cent. of the amount of water present as vapour. Taking the mean value of about 5 per cent., we find that in a fog at 5° C. the amount of liquid water per cubic metre is 0·35 grammes.

Fogs formed by the motion of warm air over a cold surface have a mean motion of about 5 to 7 metres per second. True radiation fogs move so slowly that the usual meteorological instruments fail to record their motion. It is usually assumed that radiation fogs have a motion of the order of 1 metre per second, but accurate observations of this kind are lacking.

3. The Dissipation of Fogs.

For the sake of clarity we shall assume that the fog we have to dissipate is 100 metres deep, and moves at a rate of 1 metre per second, and that the clear space which it is desired to form shall be 100 metres wide, at least initially.

Any method of dissipating the fog which shall have any practical value must act rapidly through the whole depth of 100 metres, otherwise the cleared space will take the form of a tunnel sloping upward through the fog.

The methods of dissipating fog which have been put forward may be summarised under four heads, as follows :—

(a) The electrical method, which consists in subjecting the air to a very strong electrical field, preferably a brush discharge. There is no reason to suppose that this method could ever be effective in clearing such volumes of air as would be involved in any practical dissipation of fog.

(b) The mechanical method, which would bring down to the surface fog free air from above. The assumption that the removal of fog-laden air from the surface layers by suction would suffice to bring down from above clear air to replace it, does not appear justifiable, and the method has never been regarded a serious possibility.

(c) The thermal method of warming the fog until the fog-droplets are evaporated. This is considered in fuller detail below.

(d) The chemical method, which consists essentially in the removal of sufficient water vapour from the air which carries the fog droplets to ensure the subsequent evaporation of the droplets. This method is discussed more fully below.

4. The Thermal Method.

This method appears at first sight very promising, since the total amount of liquid water in a 100 metre cube is only 350 kilogrammes. To evaporate this will require about 2×10^8 gramme calories, or say 8 therms, which, if taken from the domestic gas supply, would only cost about five shillings. In practice, it would be impossible to warm the whole depth, without bringing the vertical temperature distribution to the adiabatic, with temperature decreasing with height at the rate of 1° C. per 100 metres. To produce this temperature distribution would require another 36 therms, making a total of say 44 therms. It thus appears that the expenditure of 44 therms would suffice to clear a space

100 metres × 100 metres in a fog 100 metres deep. This space would slowly fill up again with fog as the result of the diffusion of foggy air laterally across the boundaries. If the fog had a general movement, the clear space would be carried away downwind, at the rate of 1 metre per second in the typical fog we specified above.

If the fog had a general motion of 1 metre per second, foggy air would cross the windward boundary of the space to be cleared at the rate of 10^4 (metre)^3 per second. If this air were heated as it crossed the boundary, sufficiently to clear it of fog-droplets by evaporation, heat would have to be expended at the rate of 0.44 therms per second, say 27 therms per minute. The air cleared of fog would move downwind at the rate of 1 metre per second, and the effect would be to produce a clear space which would be 100 metres wide at the windward edge, becoming narrower as it proceeded downwind. I estimate that in a light wind the width of the clear space would be about 50 metres at a distance of 600 metres from the windward edge, at which the heat is applied. Computing the cost on the basis of the use of gas, we find that the cost of forming such a clear space and maintaining it clear for a further ten minutes would be about £35, which is small by comparison with the aircraft which might be saved by landing in such a space.

The difficulty of applying this method consists in the fact that it is not possible *a priori* to work out the best way of applying the heat to the foggy air. No individual element of air must be heated to a temperature very far above that of its immediate surroundings, otherwise its buoyancy will carry it up through the fog so rapidly that its excess of heat is merely wasted. The burning of gas at the rate of 5400 cubic feet per minute, over a front of 100 metres, is not the simple problem it appears at first sight.

It would be easier to produce the necessary amount of heat by burning petrol, methylated spirit, or some other liquid, in troughs suitably distributed. Experimental work would have to be done to determine the best distribution of the sources of heat. Dr. C. F. Brooks, an American meteorologist, has described in his book entitled *Why the Weather*, a successful attempt to burn a hole in a fog over an aerodrome by burning two 50 gallon barrels of petrol poured on the aerodrome. When the fire had died down there appeared a hole in the fog, through which an aeroplane which had been waiting for it was able to land.

5. The Chemical Method.

The formation of fog requires an atmosphere containing suitable nuclei on which condensation can take place. The appearance of the fog is preceded by a fall of temperature, and an increase in the relative humidity, until a stage is reached at which condensation takes place upon the nuclei. The precise value of the relative humidity at which condensation begins depends on the nature of the nuclei, being lower for very hygroscopic nuclei than for the less hygroscopic.

Recent work carried out by Bowes and Houghton at the Massachusetts Institute of Technology has aimed at dissipating fog by destroying the equilibrium between the fog particles and the surrounding medium. In this work, a very hygroscopic substance, calcium chloride, is introduced into the foggy air, with a view to reducing the relative humidity of the air in which the water droplets are suspended below the limit at which condensation could begin on the original nuclei. This destroys the

equilibrium between the fog particles and the medium in which they are suspended, with the result that the fog particles evaporate.

In a laboratory experiment an artificial fog was prepared, and sprayed with small drops of saturated solution of calcium chloride. The results of this trial were so promising that it was considered worth trying out the method in a large scale experiment. Full details are not available of the large scale experiment, but it appears that it was carried out on a sea fog, a type of fog which drifts inland from the sea, but does not as a rule penetrate far inland. The saturated solution of calcium chloride was sprayed over a front of 100 feet from horizontal pipes set 30 feet above the ground, so that the drops of the solution fell through the fog, and in so doing scoured the air of its water vapour. The clear air formed by the evaporation of the fog droplets was carried forward by the wind, and the result was that a lane of clear air appeared in the fog, 100 feet wide and extending about 2000 feet downward. The initial visibility in the fog was 300 feet.

Little more than these bare facts have been published, and few details are available as to the visibility before, during, and after the spraying. Such observations are indispensable if we are to form a clear idea of the extent to which the apparent clearing was really due to the spraying of solution of calcium chloride. We are definitely not in a position to say that the one trial which has been reported in the Press was carried out under typical conditions.

There are at least three aspects of the problem of the dissipation of fog by chemical means which deserve consideration. In the first place, the nature of the nuclei on which the fog droplets are originally formed is of fundamental importance, since their nature determines the relative humidity at which condensation will begin, and therefore also determines the relative humidity to which it is necessary to dessicate the air between the fog droplets in order to produce evaporation of the droplets. It has usually been supposed that in a city fog the nuclei are more numerous and more highly hygroscopic than in a country fog, and that therefore the city fog is a dense cloud of very fine drops in an atmosphere whose relative humidity may be well below saturation, while the country fog consists of larger drops suspended in a medium whose relative humidity is about 100 per cent. It therefore appears safe to assume that if the relative humidity in a country or sea fog could be reduced to 90 per cent., the drops should evaporate, and the fog disappear. In a city fog, however, it would be necessary to reduce the relative humidity of the air to a much lower figure than 90 per cent., possibly to 70 per cent., in order to produce complete evaporation of the fog droplets.

In the second place, the choice of the most suitable substance for spraying the foggy air has to be considered. For the purpose of experiments on feasibility of fog dissipation calcium chloride is effective, though it has considerable disadvantages as a final solution of the problem. Calcium chloride, on account of its acid properties, is a highly corrosive substance, and it can hardly be regarded as a suitable substance to distribute widely over an aerodrome, or any other locality where machinery of any kind is exposed.

In the third place there is the question of the amount of the spray to be used, and the method of distribution. The amount of calcium chloride in the dry state required to reduce the relative humidity of the air in a space formed by a 100 metre cube from 100 per cent. to 90 per cent. is 140 kilogrammes. Or if, as in § 4 above, we consider the fog to

move at the rate of 1 metre per second, and distribute the salt at the windward edge of the space to be cleared in such a way as to clear the air of its fog as it crossed this edge, it is found that the dry chloride must be sprayed at the rate of 84 kilogrammes per minute. Using saturated solution of calcium chloride instead of the dry salt, 300 kilogrammes of saturated solution of the salt must be sprayed per minute.

The most serious problem which arises in this method of fog dispersion is the mechanical one of the distribution of the hygroscopic agent. At first sight, anhydrous calcium chloride appears to have a great advantage in that it reduces the weight of substance to be sprayed to the lowest possible value. But on account of its hygroscopic quality the dry salt is difficult to store, and probably difficult to distribute without its clogging any apparatus used in the process. The saturated solution has the advantage that no very special precautions are necessary in storing it, but for its distribution in an effective way it is necessary to determine the optimum size of drop, and to evolve a jet capable of emitting drops uniformly of that size.

It appears to be unlikely that any method can be evolved for the dissipation of a fog in which there is no definite wind, since the dissipation would involve the distribution of the chemical agent (or of heat if the thermal method were used) over the whole of the area to be cleared. When the fog has a definite motion in a direction which is determinable, it is only necessary to distribute the chemical agent (or heat) along the windward edge of the space to be cleared. This is still a difficult problem to solve, but it should be possible to get some definite result by experiment even if the method of distribution fell short of perfection.

Brief descriptions of the work done in America in developing the chemical method of fog dissipation are given in the following papers :—

(1) " A method for the local dissipation of natural fog," by E. L. Bowles and H. G. Houghton (Jnr.), *Miscellanea of the American Philosophical Society*, 16th September, 1935.

(2) In Technology Review, October, 1934, p. 20, *et seq.*, is given a semi-popular account of the work done by Houghton on the scattering of radiation in fog, and on fog dissipation.

GENERAL DISCUSSION.

Mr. C. F. Goodeve (*London*) said : If this paper covers the present position of the practical dissipation of fogs, one is led to the conclusion that very little progress has been made. There seem to be many important questions still unanswered, only a few of which are indicated below.

In the calculation of the amount of gas required to evaporate the liquid droplets, no mention is made of the necessary temperature increase of the air. What effect on the cost would this have ? The burning of gas or organic fuels produce water vapour and perhaps will do more harm than good ? If a fog is dissipated, there is an increased loss of heat by radiation. Has any estimation of this loss been made ? Have any calculations of the economic aspects of using calcium chloride been made ? Could not fountains be used to avoid the erection of dangerous apparatus ? Could the calcium chloride solution be cooled to increase its efficiency ? If it were caught in a trough system, could not a cyclical process be operated ? There are now standard methods for the economic control of humidity in factories by using refrigerating plant. Could not these methods be considered for the removal of fog ?

Dr. R. Lessing (*London*) said that from experience with a coal cleaning process employing calcium chloride on a very large scale he could confirm that there was no danger of corrosion. He anticipated, however, that calcium chloride spraying on aerodromes would not be permissible as this electrolyte would coagulate the clay in the soil and inhibit the growth of grass, thus making the surface unsuitable for traffic on the ground.

Mr. W. Barrett (*Gerrard's Cross*) said : Heat could be applied to remove fog from aerodromes by buried networks supplied with low voltage current, as already done in horticulture. It seems also worth considering whether a cloud of drops of the order of 60μ radius could be laid down on the windward edge of the belt to be cleared, so as to bring down the fog particles. The cloud particles should be colder than the fog to avoid evaporation and subsequent condensation on fresh nuclei.

Dr. B. W. Bradford (*Billingham*) said : Attention may be drawn to work carried out in America on the dissipation of clouds by spraying with electrified sand from an aeroplane, in which excellent results were claimed. The economics of the method have not been investigated—it is probably expensive—but it might be applicable to special cases such as the dissipation of fog over estuaries, or of smoke screens or toxic smokes in warfare.

Dr. R. Meldau (*Berlin*) said : The idea of settling fog by dropping electrically-charged sand from aircraft has already been tried, but with the opposite effect.[1] Indeed, in this way Veraart brought about the *formation* of clouds and mists. Probably the Americans used one polarity and the Dutch the other ; both made use of sands containing different size particles. Süring does not consider the Dutch method to be very hopeful. The experiments do not appear to have been followed up.

Dr. N. Fuchs (*Moscow*) (*communicated*) : Experiments on rain-precipitation from the clouds by spraying calcium chloride on them from an airplane were recently made in U.S.S.R. For the most part, only structural changes in the clouds were observed after this operation, namely a clearing along the path of the airplane, the tearing of the cloud into several parts, etc. But in some cases a rainfall was actually obtained. At first the rain-drops were small, and their calcium chloride content high, but later on the drop-size increased and the rain was pure water.

Professor D. Brunt (*London*), in reply, said : My paper was not meant to be encyclopædic, as Mr. Goodeve would appear to suppose. A number of points not mentioned in the paper, including those raised by Mr. Goodeve, were considered, and omitted from the paper as irrelevant to the main question. The necessary temperature increase of the air involved in the evaporation of the fog is allowed for in the estimate of heat required, and is shown in the first paragraph of section 4 of my paper to be $4\frac{1}{2}$ times the amount of heat required to evaporate the liquid water. The addition to the amount of water vapour present, involved in the use of liquid or gas fuel, is relatively small, and makes no essential difference to the estimates of cost which I gave. The increase in the loss of heat by radiation will not lead to any appreciable complication during an interval of time such as is aimed at in clearing fog. It has not been suggested that calcium chloride should be regarded at present as more than a suitable substance for experiments, and any calculations on the economic aspect of the choice of this particular compound appear a little previous. The suggestion of using fountains is quite impracticable. Drops of a size sufficiently small to present a reasonable amount of surface area to the air could not be sprayed up to heights such as are necessary for fog-clearing. The possibility of using a cyclical process such as Mr. Goodeve suggests might be considered at a later stage, but the first question is to decide whether the chemical method is at all feasible and effective. Methods involving the use of refrigerating plant, which may be effective in a closed vessel, or even inside a building, will not of necessity work in the open air.

[1] See A. Veraart, *Het kunstmatig verwekken van Regen*, N.V. Dr. Zuid-Holl. Boek-en Handelsdrukkerij, Gravenhage, 1930.

I now agree that I was mistaken in supposing that calcium chloride is corrosive, but this only removes one of several objections to the use of this substance.

Dr. Barrett's suggestion of using low voltage current to heat the air has never been tried, as far as I know. I cannot say how rapidly the heat from such a network would spread upward. A rapid diffusion of heat upward is not so necessary in horticulture, and the success of this method in horticulture does not of necessity mean that it would be effective in dissipating fog. Only an actual trial could determine the utility of the cloud of cold drops laid to windward of the area to be cleared.

The evidence as to the utility of electrified sand is so contradictory that it is impossible to assess its value.

The experiments described by Dr. Fuchs are puzzling, and it is far from obvious why the later stage of the experiments should give the precipitation of pure water.

VARIATIONS IN THE ATMOSPHERIC DUST CONTENT DUE TO MICRO-ATMOSPHERIC INFLUENCES.

By Robert Meldau (*Charlottenburg*).

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Holmes and his co-workers, in a report [1] by the American Committee of investigation on the smoke distribution from the Selby Copper Works in Montana (1915), first drew attention to the variable distribution of the smoke into regions. They marked "smoke routes" on a map (Table VI.) and established numerically that both the sulphurous acid content of the air and the arsenic and lead content of the soil were greatest at quite unexpected places in the region, namely, at 2·2 km. and 5·5 km. respectively from the chimney-stack. From the map, we may assume, without being able to particularise, that these phenomena are occasioned by a special configuration of the region, especially by locally restricted variations in the humidity (sea-shore, creeks).

If we insert numerically in the maps of the large towns, the measurements of the dust deposits, published by the Committee for Atmospheric Pollution, we find that the places of maximum deposition practically never coincide with the places of maximum industrial activity. The same conclusion is to be drawn both from the measurement of the annual dust deposit—as for example, in the town of Halle (Fig. 1)—and from the instantaneous measurements of Löbner in Leipzig [2] in 1935.

Schaeferei Trotha is situated in a slightly built-up area, *Barbarastrasse* separated from the industrial centre. The dust centres in Leipzig are irregularly distributed away from the station and factories.

If we compare the very valuable map on the characteristics of the poisonous Meuse valley fogs [3] with a geographical map, we must again

[1] *Bull.* 98, *U.S. Bureau of Mines.*
[2] Alfred Löbner, *Horizontale u. vertikale Staubverteilung in einer Grosstadt,* Leipzig, 1935.
[3] Batta, Firquet and Leqclerc, opposite p. 264 of their work.

conclude that it is not possible with any degree of certainty to explain, or even less to predict, where the zones of fog concentration must lie on geographical grounds and where fatalities are to be expected. Difficulties are encountered to a still greater extent if an attempt is made to explain why the fog concentration and the fatalities do not lie in the same zone, by assigning an essential part in precipitation to the land formation.

These and many other completely independent investigations, carried out moreover, for other purposes, seem to demand the following conclusions :—

(a) At certain places, the atmospheric pollution there arising is often disseminated irregularly into regions ; wind direction and land formation do not always suffice to explain this irregularity.

(b) This irregularity is not merely a consequence of displacement of the smoke in bulk by the wind or of sedimentation during dispersal according to the size of particle, but is markedly variable.

(c) Thus fog and dust may first concentrate at unexpected places, sometimes quite remote from their place of origin.
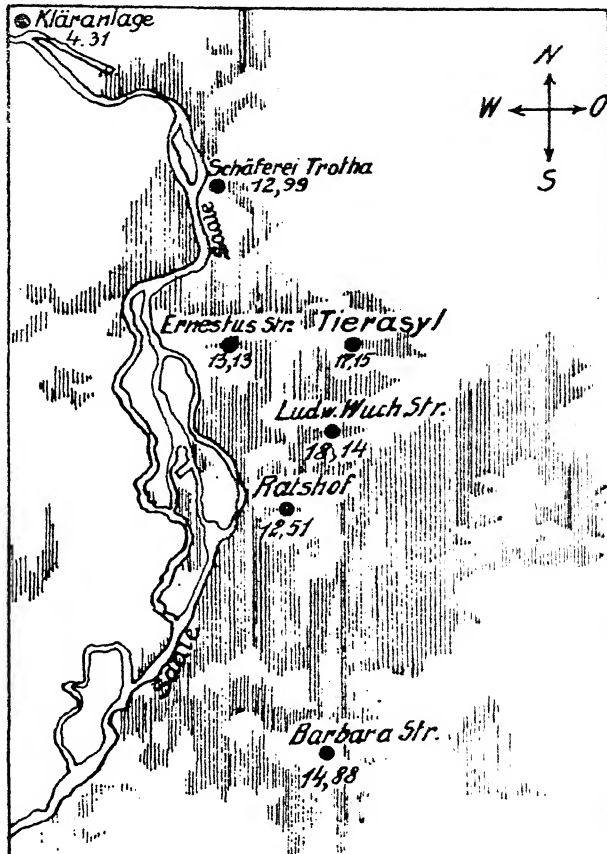
FIG. 1.—Dust deposit in Halle in 1931. (Relative values.)

The fine differences of temperature, humidity and of air currents (recently called microatmospheric) is an essential cause of this variation. Everyone who has carried out dust investigations has found that there exists not only in the open, but also in large factory rooms or assembly halls, a system of ascending and descending air currents and vortices, which, for example in closed halls, can bring about very stable zones of differentiated deposits..
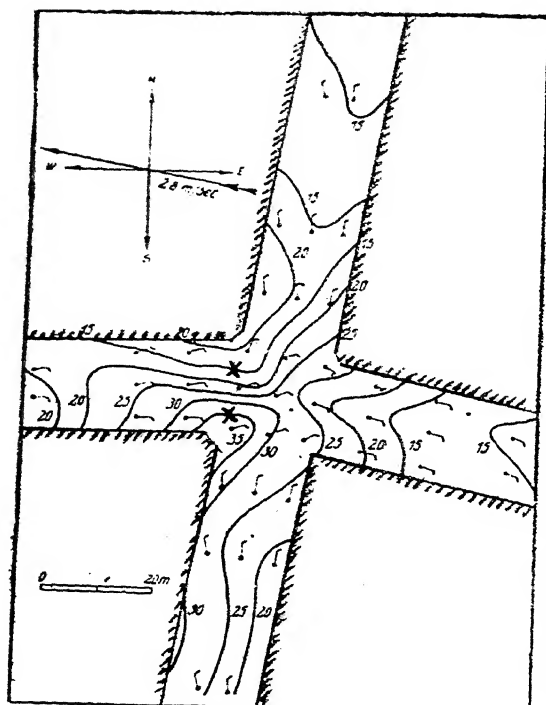
FIG. 2.—Dust distribution and wind directions at a street crossing in Leipzig (Löbner).   (Dust content in 10^3 particles per litre of air.)

Above machinery the warm air ascends, divides on reaching the ceiling and sinks, to be cooled at the external walls or windows.

The following examples may serve to show how finely distributed these microatmospheric currents are, and what differences in dust content they may effect.

Fig. 2 (Löbner [2]) shows how the dust content is distributed at a street crossing by a wind velocity of 2·8 metres per second. At the points (marked with crosses) 10 metres apart, on the right-and left-hand sides of a street, the dust content fell from 35 to 15 particles, *i.e.*, by more than 100 per cent., as a result of the slight change in angle of the direction of the street.

Fig. 3 shows the air currents and the temperatures mapped out for a Berlin street. The differences in the temperature and in the currents which contribute to the variability of the dust con-

FIG. 3.—Air-current and temperature map in a Berlin street running east-west, under the influence of a south wind of 2·7 metres/sec.

tent are clearly shown both at the ground and at higher levels.

[4] *Cp.* J. Grunow, *Der Luftaustausch der Grosstadt, Z. V.D.I.*. 1936. **80.**

GENERAL DISCUSSION.

Dr. R. Meldau (*Berlin*) (*communicated at the meeting*) : It is worthy of note that, arising from the investigations upon which Firket has reported, the lines of equal dust content in open country do not coincide with the contour lines. I am indebted to Firket for showing me a diagram containing the measurements. It follows from the fact that such accretions and decretions of dust occur, that microanalysis of industrial dust should have exceptional significance, because it makes it possible to say whether a particular dust has originated from a particular source. As a result of extended experiments, I have demonstrated that such microanalysis can, in large measure, be utilised morphologically. The differentiation of the dusts may lie in their external shape, and surface condition, in their colour, reflectivity, or refractivity, or in their internal structure. These differences can readily be noted micrographically, especially if natural colours are used.[1] (The author then showed on the screen a small selection of his microphotographs.)

Mr. W. Barrett (*Gerrard's Cross*) said : Associated with wind, especially with gusty wind, are rapid variations of pressure. The air in a heap of dust responds to these and so the top particles are lifted into the system of eddies described by Dr. Meldau. It is probably for a reason of this nature that, under a falling barometer, dust is more readily lifted than at other times and this gives a physical explanation of the popular saying that blowing dust commonly foretells rain.

Dr. R. Lessing (*London*) called attention to the eddies produced in wind by buildings of even moderate height, and cited the case of an anemometer at a coastguard station on the Atlantic coast, the irregular working of which was traced to a cottage some distance away interfering with the streamline flow of the wind.

Dr. R. Meldau (*Berlin*), in reply, said : Settled dust is frequently lifted again. How settled dust may be lifted again from soil has been studied in the case of the sand-hills and of the ripple marks on sands, both in theory as in practice.

[1] See Meldau, *Archiv. Wärmewirtschaft*, 1930, 281 ; *ibid.*, 1931, 304 ; *Z.V.D.I.* 1931, 1467 ; 1935, 356 ; Stach, *Z.V.D.I.*, 1935, 513 ; Molisch, *Pflanzenchemie und Pflanzenverwandschaft*, Fischer, Jena, 1931.

THE ENERGY EFFICIENCY OF IONISATION IN ELECTRICAL PRECIPITATION.

By C. A. MEEK AND R. WINSTANLEY LUNT.

1. Introduction.

In the phenomenon of electrical precipitation of dusts and mists it is possible to distinguish at least three main processes which lead ultimately to the precipitation of the particles :

(i) The ionisation of the gas in which the dust or mist particles are suspended.

(ii) The transfer of electric charge to dust or mist particles in collisions between these particles and electrons, positive ions,

and negative ions; the ions concerned being those derived from the molecules of the carrier gas.

(iii) The motion of charged dust or mist particles due to the electric field between the electrodes.

In this paper we shall be mainly concerned with process (i). We shall consider firstly the general character of the process of ionisation of the carrier gas, particularly in its relation to the Townsend coefficient of ionisation, the electric field, and the pressure of the carrier gas. After noting the main characteristics of the type of discharge used in electrostatic precipitation, we shall then consider how far the conditions in such discharges depart from the optimum for effecting the ionisation of the carrier gas.

2. The Townsend Coefficient of Ionisation.

It was shown by Townsend [1] that if a constant current of electrons, i_0, be liberated from the surface of a (plane) metal electrode (for example, by allowing a beam of ultra-violet light to fall on it), and if a constant electric field be maintained between this electrode and some other plane electrode so that the electrons tend to move away from the surface at which they are liberated, then for any given pressure of gas in the space between the electrodes, the dependence of the total current flowing between the electrodes, i, and the distance between them, x cms., is given by

$$i = i_0 e^{\alpha x}, \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

where α is a constant. Townsend interpreted this exponential growth of the current with the distance between the electrodes by supposing that the electrons leaving the cathode acquire sufficient energy from their motion in the field to enable them to ionise the gas molecules in collisions, the electrons formed simultaneously with the ions performing similar collisions. He showed that α is a measure of the ability of the electrons to ionise, and is defined as the average number of ions generated (or of ionising collisions suffered) by an electron per cm. of its drift * motion in the direction of the uniform electric field between the electrodes; he termed α the coefficient of ionisation.

Numerous determinations, mainly by Townsend and his collaborators,[2] have shown that, in a given gas, αp^{-1} is a function of the ratio $X p^{-1}$, where X is the strength of the uniform field between the electrodes, and p the gas pressure; by convention X is expressed in volts cm.$^{-1}$, and p in mm. Hg, so that $X p^{-1}$ is expressed in units of volts cm.$^{-1}$ mm. Hg^{-1}. An important point concerning these experiments to determine αp^{-1} is that the current density was very small, being of the order of 10^8 electrons cm.$^{-2}$ sec.$^{-1}$ and that the pressure rarely exceeded 50 mm. Hg.

It is found that the dependence of αp^{-1} on $X p^{-1}$ can be expressed to a close approximation by the empirical † expression over a wide

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[1] Townsend, *Electricity in Gases*, Oxford, 1915, Chap. VIII.

* The actual motion of the electrons is, of course, largely random; it is customary to speak of the component of the total motion in the direction of the electric field as the " drift " motion.

[2] Summarised in Knoll-Ollendorf-Rompe, *Gasentladungstabellen*, Leipzig, 1934.

† A theory of Townsend [1] which attempted to provide a theoretical basis for this expression is now recognised [3] to be based on untenable hypotheses.

[3] *Cf.*, for example, Mierdel, *Handb. d. Experimental Physik*, vol. XIII., part 3.

range of Xp^{-1}

$$\alpha p^{-1} = k_1 e^{-k_2 p X^{-1}}, \qquad . \qquad . \qquad . \qquad . \qquad (2)$$

where k_1 and k_2 are constants characteristic of the gas concerned.

A quantity related to α is the energy efficiency of ionisation, η; this is defined as the average number of ions generated per electron-volt of energy supplied from some external source to maintain the discharge in which the ions are being produced. From the definition of α, it follows that the average energy gained by an electron from the field, X, whilst it produces α new ions, is simply X electron-volts, or

$$\eta = \alpha . X^{-1} \qquad . \qquad . \qquad . \qquad . \qquad (3)$$

Since $\qquad \alpha . X^{-1} = (\alpha p^{-1}) . (Xp^{-1})^{-1} \qquad . \qquad . \qquad . \qquad (4)$

it follows that η is also a function of Xp^{-1}, and that values * of η may at once be computed by means of (4) from the published data for αp^{-1} and the corresponding values of Xp^{-1}. On substituting the approximate empirical expression for α in (3) we find that η will be approximately represented by

$$\eta = k_1 . pX^{-1} . e^{-k_2 p X^{-1}}. \qquad . \qquad . \qquad . \qquad (5)$$

From this it follows that a single maximum, η_{max}, is to be anticipated for η considered as a function of Xp^{-1}, and that this maximum value will be attained when

The data for η in air derived from the published data for αp^{-1} are shown in Fig. 1, from which it is seen that this quantity passes through a well-defined maximum, $1 \cdot 45 \times 10^{-2}$ ions per electron-volt for $Xp^{-1} = 400$.

Whilst little attention appears to have been paid previously [4], [5] to η or αX^{-1}, it must be pointed out that long ago Townsend [1] recognised that the point of inflexion in the curves of αp^{-1} as a function of Xp^{-1} provided the explanation for the Stoletow effect, and, of course, the existence of such a point of inflexion is formally identical with a maximum in αX^{-1}. What does not appear to have been fully recognised until recently is that αX^{-1} (or as we shall refer to it henceforth, η) is an *energy efficiency* for the production of ions.†

Since η, the energy efficiency for the production of ions of the carrier gas, is clearly a matter of importance in any process of electrical precipitation, it is pertinent to enquire, firstly, how far this dependence of η on Xp^{-1} may be anticipated to remain valid in the corona discharges used in electrical precipitation, secondly, what are the values of Xp^{-1} in these discharges, and thirdly, how far the values of η for the usual corona conditions diverge from the maximum.

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* The relation to convert η ions per electron-volt to practical units, A gms. of ions per K.W.H., is

$$A = 37 \cdot 4 . M . \eta,$$

where M is the molecular weight of the ion concerned.

[4] Townsend and McCallum, *Phil. Mag.*, 1934, **17**, 678.

[5] *Cf.*, for example, *ibid.*, 1934, **17**, 678.

† Von Engel and Steenbeck [6], [7] have discussed the importance of the related quantity $X\alpha^{-1}$, the average energy expended per ion produced.

[6] Steenbeck, *Z. Physik*, 1929, **53**, 192.

[7] Von Engel and Steenbeck, *Elektrische Gasentladungen*, Berlin, 1932, p. 93.

3. The Dependence of   on Xp^{-1} in a Corona at Atmospheric Pressure.

It has already been mentioned that, in the experiments of the Townsend school to measure αp^{-1}, the current density was extremely low, and the pressures of the order of a tenth of an atmosphere, or less. The first important application of these data to other conditions was Townsend's prediction of the sparking potential between parallel plates in gases at the same range of relatively low pressures.[8] The success attending this prediction indicates that the values of αp^{-1} are still valid for the current density *immediately preceding the breakdown;* whilst such current densities must be considerably greater than those in the
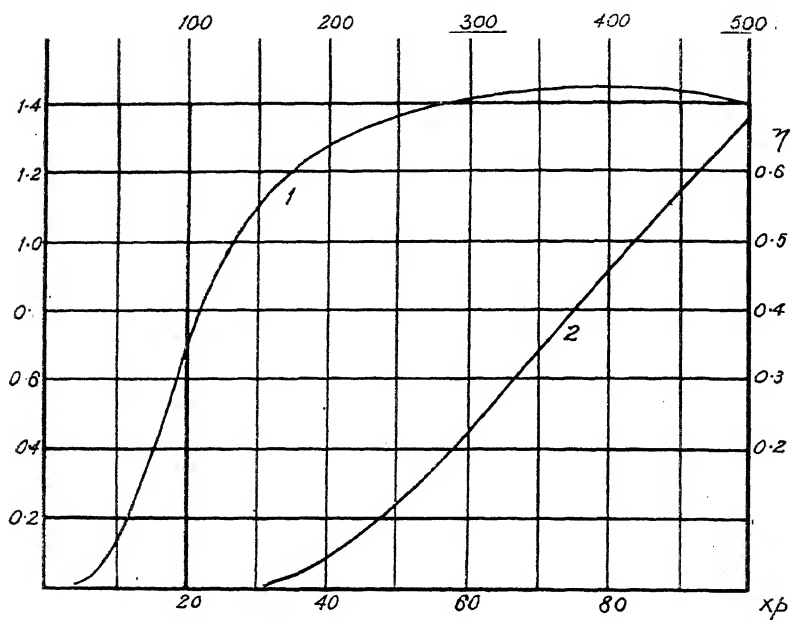
Fig. 1.—The energy efficiency of ionisation in air, η.
Curve 1, left hand and top scale; curve 2, right hand and bottom scale.

experiments to measure αp^{-1}, they must be less than those in a discharge maintained solely by the potential between the electrodes * (no measurements of the current density in the transition stage appear to have been made). In considering the experimental data for the sparking potential between parallel plates (and other shapes of conductors) at atmospheric pressure, Schumann,[9] by using a simplified form of the Townsend condition for breakdown,[8] came to the conclusion that the dependence of αp^{-1} on Xp^{-1} was no longer represented by (2). He proposed several

[8] Townsend, *op. cit.*, Chap. IX.
* That is a " self-sustaining discharge "; in the experiments to measure αp^{-1} the current is maintained by the photo-electrons ejected at the cathode and by the interelectrode field.
[9] Schumann, *Elektrische Durchbruch feldstarke von Gasen*, JuliusSpringer, Berlin.

empirical formulæ, finally reaching the conclusion that the best of these was

$$\alpha = A \cdot \mathbf{X}^{-2} \cdot \exp\left(- B \cdot \mathbf{X}^{-2}\right), \qquad . \qquad . \qquad (7)$$

where A and B are positive constants, and $\mathbf{X}$ is the field strength * in kV. cm.$^{-1}$. Since the pressure is now constant (atmospheric) it does not appear in (7). Some idea of the empirical nature of this expression may be gained by noting that Schumann [9] selects values of A and B for a particular electrode configuration. The corresponding value of the energy efficiency, which we will denote by η_s, then follows as

$$\eta_s = \mathrm{10}^{-3}\alpha \cdot \mathbf{X}^{-1} = \mathrm{10}^{-3}A \cdot \mathbf{X}^{-3} \cdot \exp\left(- B \cdot \mathbf{X}^{-2}\right). \qquad . \qquad (8)$$

It is interesting to note that η_s also passes through a maximum as $\mathbf{X}$ (and hence Xp^{-1}, since p is now constant) progressively increases; by differentiating (8) it can easily be shown that $\eta_{s,\,\mathrm{max}}$ occurs when $\mathbf{X} = (2B/3)^{0\cdot5}$, or

$$Xp^{-1} = (\mathrm{10}^3/760)\mathbf{X}. \qquad . \qquad . \qquad . \qquad (9)$$

The actual values of η_s cannot be computed from (8) because A is an unknown constant; we can, however, evaluate η_s/A which is proportional to η_s. By using Schumann's values for a wire-in-cylinder electrode configuration, $B = 6300$, it is found that $\eta_{s,\,\mathrm{max}}$ occurs at $\mathbf{X} = 65$ kV. cm.$^{-1}$, or $Xp^{-1} = 85$. It is a little difficult to estimate the weight that Schumann himself attaches to the values of α given by (7), for, although he points out that these lead to a satisfactory (but empirical) interpretation of the phenomena of breakdown, he also points out that, for the above value of B, expression (7) predicts that α itself will pass through a maximum for $\mathbf{X} = B^{0.5} = 79\cdot5$ kV. cm.$^{-1}$, and of the existence of this maximum he expresses considerable doubt.

The next developments come from the Rogowsky school where Paavola [10] showed that direct determinations of αp^{-1} in air at atmospheric pressure by a modified form of the Townsend [1] technique are in substantial agreement with the values predicted from (2), using values for the constants k_1, k_2 derived from measurements of the Townsend school [2] at much lower pressures; these results were confirmed later by Masch.[11] It was then shown by Rogowsky that the use of these values of αp^{-1} in a modified theory of breakdown led to predictions of the actual conditions of breakdown in good agreement with experiment.[12] If Rogowsky's theory be accepted, then his results show that the values of αp^{-1} given by (2) are valid for atmospheric pressure and for current densities up to the value immediately preceding breakdown: again, although the absolute magnitude of this limiting current density is not known, it must be less than that in the discharge which follows. It then appears that Schumann's success in accounting for breakdown phenomena by using values of α given by (7) and a simplified form of Townsend's condition for breakdown must be attributed to mutually compensating errors; it follows that the values of η_s given by (8) are open to considerable suspicion.

In the absence of any other relevant further experimental data, it is necessary to glance at the theory of the Townsend coefficient α in

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* On account of the high field encountered in discharges at atmospheric pressure, it is customary to express these in kV. cm.$^{-1}$, and for that we shall use the distinguishing symbol $\mathbf{X}$ where $X = \mathrm{10}^3\mathbf{X}$.

[10] Paavola, *Arch. f. Electrotech.*, 1932, **26**, 443.

[11] Masch, *ibid.*, 1932, **26**, 587.   [12] Rogowsky, *ibid.*, 1932, **36**, 643.

order to attempt a prediction of the continued validity of the dependence of αp^{-1} on Xp^{-1} in the still greater current densities of an actual corona discharge.

4. The Theory of the Townsend Coefficient α.

Emeleus, Lunt, and Meek [13] have recently shown that the theory of an electron swarm moving in a gas under the influence of a uniform electric field leads to the following expression for αp^{-1}:—

$$\alpha p^{-1} = W^{-1} . k . M(\bar{V}), \qquad . \qquad . \qquad . \qquad (10)$$

where W is the average electron drift velocity in the direction of X and is known as a function of Xp^{-1} from the work of Townsend and his collaborators,[8] k a numerical constant $= 1.86 \times 10^8$, and

$$M(\bar{V}) = \int_0^\infty Q_i(V) . V^{0.5} . f(V) . dV. \qquad . \qquad . \qquad (11)$$

In (11) $f(V)dV$ is the energy distribution function for the electrons in the swarm and must be a function, $F(\bar{V})$, of the average electron energy, $\bar{V}$; $\bar{V}$ is known from the work of the Townsend school [14] to be a function of Xp^{-1} for low current densities and gas pressures comparable to those used in the determination of αp^{-1}. The expression $Q_i(V)$, the probability cross-section for ionisation by an electron of energy V electron-volts, is the quantity determining the probable number of ionising collisions made by an electron of energy V per cm. of its (actual *) path through a gas. Since $f(V)dV = F(\bar{V}) = F_1(Xp^{-1})$ by experiment, and since $W = F_2(Xp^{-1})$ also by experiment, it follows from (10) and (11) that αp^{-1} is predicted by this theory also to be a function of Xp^{-1}.

By using the data of Townsend [14] for the dependence of W and $\bar{V}$ on Xp^{-1}, the data of Tate and Smith for $Q_i(V)$,[15] and by making the assumption of a Maxwellian form † for $f(V)dV$, it is found that, for hydrogen and certain other molecular gases including air,‡ the values of αp^{-1} (and therefore also of η) calculated from (10) are in good agreement with experiment. This agreement between theory [13] and experiment is evidence that the only assumption involved, that of a Maxwellian electron energy distribution, must represent § very closely the actual distribution in the experiments in which αp^{-1}, W and $\bar{V}$ were determined as functions of Xp^{-1}. But the theoretically calculated values of αp^{-1} are also in satisfactory agreement with the experimental values determined *at atmospheric pressure*,[10, 11] for which there are no corresponding data for the dependence of W and $\bar{V}$ on Xp^{-1}. At this pressure there are therefore three assumptions ¶ in volved in calculating αp^{-1} from

[13] Emeléus, Lunt and Meek, *forthcoming paper in Proc. Roy. Soc.*

[14] Townsend, *The Motion of Electrons in Gases*, Oxford, 1925.

* The velocity W is the component of the actual velocity in the direction of the field X.

[15] Tate and Smith, *Physic. Rev.*, 1932, **39**, 270.

† *I.e.*, $f(V) . dV = (27/2\pi)^{0.5} . V^{0.5} . e^{-1.5V/\bar{V}} . d\bar{V}$.

‡ Since there are no $Q_i(V)$ values for air, an approximate expression, based on that valid for other gases; this takes the form $Q_i(V) = A . (V - V_i)$ where V_i is now the " effective " ionisation potential [2] of air, 16·3 volts.

§ Although the assumption of this distribution effects the correlation between experiment and theory, there is no proof that it constitutes a unique solution, although this is highly probable for other reasons.[13]

¶ It is now necessary to assume, in addition to the Maxwellian nature of the distribution function, that the dependence of W and $\bar{V}$ on Xp^{-1} is the same as that measured at much lower pressures.

(10) and (11): whilst it is, of course, possible that the observed agreement with experiment may be due to mutually compensating errors, it is more reasonable to conclude that the dependence of W and $\bar{V}$ on Xp^{-1} at atmospheric pressure is sensibly the same as that observed at lower pressures, and that the electron energy distribution is still Maxwellian. This conclusion relates necessarily to the relatively low current densities for which αp^{-1} was determined at atmospheric pressure.

It remains to consider whether this dependence of W and $\bar{V}$ on Xp^{-1} and the distribution function may be anticipated to remain unchanged in the *considerably higher* current densities of corona discharges at atmospheric pressure. The early experiments of Wilson [26] indicate that the values of W in positive column discharges in air at low pressure are of the same order of magnitude as those determined for much lower current densities. Whilst there is no evidence for discharges at atmospheric pressure, a related case with which comparisons may be made is that of the formation at atmospheric pressure of ozone from oxygen in ozoniser discharges ; this form of discharge is essentially a capacity limited corona. Lunt and Meek [16] have calculated by expressions formally similar * to (10) and (11) the energy efficiency for the formation of ozone from oxygen as a function of Xp^{-1} in fair agreement with experiment. In performing these calculations it has been assumed, in addition to the existence of a Maxwellian electron energy distribution, that the dependence of W and $\bar{V}$ on Xp^{-1} *for oxygen* at atmospheric pressure is the same as that measured [14] at much lower pressures. Whilst this result might again be due to mutually compensating errors, it suggests strongly that the assumptions involved are correct. If this conclusion be accepted then it is reasonable to infer that it may also be anticipated that, also *in the case of air* in a discharge at atmospheric pressure, the electron energy distribution is sensibly Maxwellian, and the dependence of W and $\bar{V}$ on Xp^{-1} is sensibly the same as that measured [14] at much lower pressures. It then follows that the dependence of η on Xp^{-1} given in Fig. 1 may also be anticipated to remain valid in the conditions of atmospheric corona.

There is ample experimental evidence from probe data that, discharges at low pressure the electron energy is frequently Maxwellian,[17] at least to a close approximation ; and Druyvestyn has recently pointed out in a theoretical investigation of the distribution function [18] that, on account of the interaction between ions and electrons, the distribution for the high. current densities of a self-maintained discharge (of which corona is one example) must approximate closely to the Maxwellian.

Summarising this discussion of the actual values of αp^{-1} and η at atmospheric pressure for low current densities, and their continued validity in a corona discharge, we see, firstly, that the direct determinations of Paavola [10] and Masch [11] for low current densities indicate that no great reliance can be placed on the values given by the empirical expression of Schumann. Secondly, that although there is no direct evidence for the continued validity of these values in corona discharges, there are many lines of argument which indicate that this is probably the case.

[16] Lunt and Meek, *unpublished work.*
* That is, expressions in which $Q_i(V)$ is replaced by the corresponding quantity for the excitation and subsequent dissociation of molecular oxygen by electron impact.
[17] Compton and Langmuir, *Rev. Mod. Physics.*, 1930, **2,** 1 ; *ibid.*, 1931, **3,** 192.
[18] Druyvesteyn, *Physica,* 1936, **3,** 65.

5. The Field in a Corona Discharge.

Whilst a complete theory of the mechanism of corona discharges is still lacking, it is generally accepted that ionisation by electron impact is confined to a luminous zone, the corona itself, close to one (or both in the case of a parallel wire system) electrode. It is therefore in this zone of the discharge that it is pertinent to the practice of electrical precipitation to consider the values of Xp^{-1} and the corresponding values of the energy efficiency for ionisation of the gas, η. For simplicity we shall confine our attention to the " wire-in-cylinder " type of electrode arrangement, and, in particular, consider the case closely related to current practice, a $1/16$-inches diam. wire centrally placed with respect to a tube of 7 inch diam. ; the radius of the wire, r, is then 0·080 cm., that of the cylinder, R, 8·9 cm., and the spacing between the electrodes, a, 8·82 cm. In order to illustrate certain theoretical predictions we shall also consider the case of a larger wire diameter, $r = 0·200$ mm., in the same sized outer cylinder so that the value of a is now 8·70 cm.

Unfortunately, there appear to have been no direct determinations of the field between concentric cylinders for continuous current corona discharges since those of Booth [19] in 1917 ; and from the small scale diagrams reproduced in his paper it is impossible to estimate the field in the region of the actual corona, the diameter of which can be estimated from independent data. It is therefore necessary to approach the problem from the theoretical side, which, as has been mentioned, is far from being completely developed.

The earliest theory of the current-voltage relationship in corona discharges is due to Townsend.[20] In this it was assumed (amongst other things) that the field at the outer edge * of the corona, $\mathbf{X}_{c,\,0}$, was equal to limiting critical field for breakdown at large electrode spacings between conductors of small curvature, about 30 kV. cm.$^{-1}$ in air at atmospheric pressure ; it was also assumed that the ionisation in the corona was determined by the mean field in the corona which was itself assumed to be given by 0·5 $(\mathbf{X}_c + 30)$, where $\mathbf{X}_c$ is the critical field at the surface of the wire necessary to produce corona. The assumption that $\mathbf{X}_{c,\,0} \leftrightharpoons 30$ kV. cm.$^{-1}$ has also been used later by Peek [21] in attempting to provide an explanation for the dependence of the corona diameter on the applied voltage. In a recent investigation Prinz [22] has pointed out that the Townsend theory (together with several others) fails to predict the experimentally observed relationship between the applied potential and the power absorbed by the discharge, and that this failure is attributable, in part, to the neglect in these theories of the effects due to the field in the corona itself, and to the assumption that $\mathbf{X}_{c,\,0} \leftrightharpoons 30$ kV. cm.$^{-1}$. Prinz then develops a modified theory of corona which takes account of the field in the corona ; the great merit of this theory is that it predicts the observed potential-power relationship despite the fact that, as Prinz himself admits, it is to some extent empirical. Not merely does this theory enable calcula-

[19] Booth, *Physic. Rev.*, 1917, **10**, 266.   [20] Townsend, *op. cit.*, Chap. X.
 * The symbol X will be used to denote field strengths expressed in kV. cm.$^{-1}$, thus distinguishing them from X which refers to volts^{-1} cm.$^{-1}$.
[21] Peek, *Dielectric Phenomena in High Voltage Engineering*, 2nd edition, New York, 1932.
[22] Prinz, *Die Gleichspannungskorona*, Dr. Ing. thesis, München, 1934.

tions to be made of the field in the corona, X_x, as a function of the radial distance x, but it also leads to the conclusion that $X_{c, 0}$ is less than 30 kV. cm.$^{-1}$ by an amount depending on the geometry of the electrode system. This latter conclusion is of particular importance for electrical precipitation, because, as may be seen from Fig. 1, the lower the value of X_x (and therefore also of $X_x \cdot p^{-1}$) the lower is the value of η.

We shall now consider the application of Prinz's theory to the particular cases mentioned previously. The first relationship required is that of the dependence of the corona radius, x_0, on the applied potential V kV. For this there are no completely satisfactory data, due mainly to the fact that this radius is difficult to define; we shall rely here on the photographic determinations with quartz lenses by Whitehead [23] who found that for values of V exceeding the critical value for the commencement of corona, V_c, by more than a small amount (of the order of 5 kV.) the relation is

$$x_0 = r + K \cdot (V - V_c), \quad . \quad . \quad . \quad (12)$$

where K is a constant depending on the geometry of the system. The case investigated by Whitehead approximating most closely to that we are now considering was for $r = 0{\cdot}1165$ cm. and $R = 9{\cdot}3$ cm. ; from his data the value found for K is $0{\cdot}035$. Prinz adopts the value $K = 0{\cdot}5$ cm. kV.$^{-1}$ which is obviously impossibly high, but from the data given in his Fig. 57 it appears that the value corresponding to the other conditions stated on that Fig. is $K = 0{\cdot}0565$ cm. kV.$^{-1}$, but whether this is an experimental value is not clear. We shall adopt the experimental value $K = 0{\cdot}035$, and consider the case for a relatively large corona radius $x_0 = 1$ cm. For the values of r and R selected, the values of V_c, found from the standard (experimental) expressions,[21, 22] are approximately 25 kV. and 42 kV. respectively.

According to Prinz's theory,[22] the field at the outer edge of the corona, $X_{c, 0}$, is given by

$$X_{c, 0} = x_0^{-1}(V_c + (x_0 - r)/K) \cdot \frac{\beta - 1}{\beta(\beta - 2)}$$

$$\times \left[1 - \sqrt{1 - \frac{\beta - 2}{(p-1)^2}\beta \left\{ \frac{1{\cdot}32}{1 + \dfrac{x_0 - r}{KV_c}} - 0{\cdot}32 \right\}} \right] \quad (13)$$

where, for the case of concentric cylinders, $\beta = \log_e R/r$. After performing the calculations, it is found that for $r = 0{\cdot}080$ and $0{\cdot}200$ mm. the values of $X_{c, 0}$ are, respectively, $2{\cdot}3$ and $7{\cdot}3$ kV. cm.$^{-1}$; the corresponding values for the potential across the electrodes according to (12) are $V = 50$ and 65 kV. respectively.

It must be pointed out that these values of $X_{c, 0}$ are surprisingly low, and until direct confirmatory evidence is available, we believe that they must be accepted with some caution. Since the wire electrode is negative, the corona itself may be regarded as a glow discharge in which, due to the high pressure, the negative zones have contracted to microscopic dimensions close to the wire, so that the main bulk of the corona will approximate to a positive column. There are unfortunately few data for positive column discharges in air, but Wilson [24]

[23] Whitehead, *Proc. A.I.E.E.*, 1912, **31**, 839.
[24] Wilson, *Proc. Camb. Phil. Soc.*, 1902, **11**, 249, 391.

in 1902 showed that at low pressures, and for current densities comparable to those in corona at atmospheric pressure

$$Xp^{-1} = 35 \cdot p^{-0.5} \qquad . \qquad . \qquad . \qquad (14)$$

If we assume that this relation is still valid at atmospheric pressure, the value of Xp^{-1} is 1·28 ; this result would then signify that luminous discharges would be expected to occur in air at atmospheric pressure for this value of Xp^{-1}. It will be noticed that this value is considerably below the values of Xp^{-1} corresponding to the values of $\mathbf{X}_{c,\,0}$ derived from the application of Prinz's theory, the relation between Xp^{-1} and $\mathbf{X}_{c,\,0}$ being given by

$$Xp^{-1} = (10^3/760)\mathbf{X}_{c,\,0} \qquad . \qquad . \qquad . \qquad (15)$$

We may therefore find in these results of Wilson some provisional justification for accepting the low values of $\mathbf{X}_{c,\,0}$ predicted by Prinz's hteory.

In order to calculate the energy efficiency of ionisation in the corona we require to know, firstly, the values of Xp^{-1} at the radial distance x; these follow from (15) when $\mathbf{X}_{c,\,0}$ is replaced by the $\mathbf{X}_{x}$, the field at the radial distance x, which, from Prinz's theory, is given by

$$\mathbf{X}_{x} = x^{-1} \cdot x_0 \cdot \mathbf{X}_{c,\,0}. \qquad . \qquad . \qquad . \qquad (16)$$

It is found that resulting values of Xp^{-1} inside the corona lie partly below the range in which αp^{-1} (and thence η) has been measured, $Xp^{-1} \geqq 31$. For the values of $Xp^{-1} < 31$ the data of Masch do not suggest any obvious method of extrapolation ; we have therefore made the somewhat arbitrary assumption that η has the constant value of 0·05 . 10^{-2} corresponding to the measurements at $Xp^{-1} = 31$. Some justification for this procedure is afforded by the work of Eméleus, Lunt and Meek,[13] who have concluded that at very low values of Xp^{-1} the electron energy distribution varies in such a way that the diminution of η as Xp^{-1} diminishes is not nearly so rapid as that predicted by (10) for a Maxwellian distribution. In any case, the error introduced probably leads to high rather than low values of η for Xp^{-1} less than 31. For higher values of Xp^{-1}, η has been derived from the data of Masch,[11] Fig. 1.

Since Xp^{-1} varies in the corona itself, the quantity of interest to evaluate is the average value of the energy efficiency of ionisation in the corona, $\bar{\eta}$. From the definition of η it follows that the rate of generation of ions at the radial distance x is given by the product of η and the rate at which energy is supplied to maintain the corona at this radial distance.

If I is the current in μA per cm. length of the wire-in-cylinder system, then the energy input *to the corona* per cm. length, P_c, is given by

$$P_c = 6\cdot 3 \cdot 10^{15} \cdot I \int_r^x \qquad . \; dx \text{ electron-volts }$$

or, by (16),

$$P_c = 6\cdot 3 \times \qquad \qquad \mathbf{x}_{c,\,0} \cdot \qquad \quad \cdot \; . \; dx$$

$$= 6\cdot 3 \times 10^{15} \cdot I \cdot \mathbf{X}_{c,\,0} \cdot \log_e x_0/r. \qquad . \qquad . \qquad (17)$$

Similarly, the total ionisation per cm. length, N_i ions sec.$^{-1}$, is given by

$$N_i = 6\cdot 3 \times 10^{15} \cdot x_0 \cdot I \cdot X_{c,\,0} \int^{x_0} \eta_x \cdot x^{-1} \cdot dx, \qquad . \qquad . \qquad (18)$$

where η_x is the value of η at the radial distance x.   From these expressions the average value of η may be found, and is given by

$$-1 = \int_r^{x_0} \!\!\! ,$$

The values of the integral in (16) must be found by quadrature. After evaluating this integral and P_c for the two values of r under consideration, we find for $r = 0\cdot080$ and $0\cdot200$ cm., respectively, $\bar{\eta} = 5\cdot6 \times 10^{-5}$ and $1\cdot22 . 10^{-4}$. This shows that $\bar{\eta}$ is considerably higher for the thicker wire, but is still only $1\cdot2$ per cent. of the maximum value, $1\cdot45 . 10^{-2}$ (Fig. I).

It must, of course, be pointed out that this gain in the average value, $\bar{\eta}$, by using a thicker wire is achieved at the expense of a higher operating potential.   It is therefore pertinent to consider next the overall energy efficiency, $\bar{\eta}_0$, referred to the total energy supplied to maintain the corona, P_t. Per cm. length of wire, P_t is given by

$$P_t = 6\cdot3 \times 10^{15} \, IV \text{ electron-volts sec.}^{-1}.$$

Hence from (17) and (19) the overall energy efficiency of ionisation, $\bar{\eta}_0$, is given by

$$\bar{\eta}_0 = \bar{\eta} . P_c . P_t^{-1}; \quad . \qquad . \qquad . \qquad . \quad (19)$$

the values of $\bar{\eta}_0$ derived from (19) for $r = 0\cdot080$ and $0\cdot200$ cm. are, respectively, $6\cdot55 \times 10^{-6}$ and $2\cdot20 \times 10^{-5}$.   These results show that despite the increased operating voltage, there is still a considerable increase in overall energy efficiency of ionisation to be gained by using wire of larger diameter.

Summarising this application of Prinz's theory to the conditions of electrical precipitation, the most striking result is the prediction of very low values of the (ionising) field in the corona itself.   The authors therefore believe that direct experimental determination of the field in corona would be of considerable importance, for the fact that Prinz's theory correctly predicts the dependence of the direct current corona loss on the voltage, and geometry of the system, cannot of itself be regarded as complete proof of the validity of this admittedly [22] semi-empirical theory.   The values of the average energy efficiency corresponding to these low corona fields are also extremely low compared with the predicted maximum ; the calculations for central wires of different diameters indicates that a considerable gain of efficiency of ionisation may be achieved by the use of large central wires.

6. The Effect of Dust and Mist on η.

The calculations made in the preceding section relate to air alone ; it is next necessary to enquire how far the conclusions reached there might be modified by the dust or mist present in actual precipitating conditions.   In their recent summary, Mierdel and Seeliger [25] have pointed out that the presence of dust or mist lowers the critical corona voltage and increases the corona current for a given applied voltage. These results suggest that, other things being equal, the presence of dust or mist tends to lower the field in the corona and therefore also the energy efficiency of ionisation.   As in the case of dust-free air discussed

[25] Mierdel and Seeliger, *Arch. f. Elektrotechnik*, 1935, **29**, 149.

in the previous section, no certain conclusions can be drawn until direct determinations of the field in the corona have been made when dust or mist is present.

Summary.

Reasons have been given for believing that the value of the energy efficiency of ionisation in air at atmospheric pressure determined at low current densities are valid in the higher current densities of corona discharges.

The recent theory of Prinz has been applied to·calculate the field strength in corona for conditions approximating to those found in the practice of electrical precipitation. This theory predicts that the field strength will increase with the wire diameter.

From the values of the field strength derived from the application of Prinz's theory the overall energy efficiency of ionisation has been calculated. These are found to lie far below the maximum value.

This application of Prinz's theory has revealed that further experimental work is desirable to determine the dependence of corona size on the electrical and geometric factors, and to determine the field in the corona itself.

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THE PHYSICAL BASIS OF ELECTRICAL GAS PURIFICATION.

By G. Mierdel and R. Seeliger.

It is well known that in principle electrical gas purification consists in subjecting the mixture of gas and dust to a unidirectional electric field in which an electric discharge in the form of a corona is taking place. The dust particles become charged in the latter, so that they move in the field towards one of the two electrodes where they are deposited for the most part as a firmly coherent layer. In principle, the charging and precipitation can take place in separate units, the gas stream flowing from one to the other, an arrangement which can be advantageous in many cases. In practice, however, almost without exception the two processes take place in the same apparatus, and this essentially takes one of two forms, wire-in-cylinder, or wire-and-plate.

(1) The Charging of Dust Particles in the Corona Discharge.

In gases at high pressure, which conditions alone are now relevant, it is possible to distinguish two zones in a corona discharge : there is a narrow, luminous zone in the neighbourhood of the wire electrode, the corona itself, and a completely non-luminous region which extends from the corona to the outer electrode. This visual difference between the two zones can be accounted for theoretically. In the corona there is a field distorted by space charge maintaining the discharge in a steady

state, and in which the necessary charged particles of the same sign as the wire are generated by electron collisions ("electron avalanche"). These charged particles are carried to the other electrode by the field in the non-luminous or "transport" zone. On account of the relatively small volume of the corona, the transport zone is practically the only region which is effective in charging the dust particles; a more exhaustive examination of the processes occurring in the corona is therefore only of secondary interest for the theory of charging the dust.[1]

It will suffice to consider here a negatively charged wire, and therefore negatively charged carriers, in the transport zone, for these are the only conditions found in practice; that is why *ceteris paribus*, the current for negative corona is somewhat greater than for positive, and, more important still, the breakdown potential, which sets an upper limit to the operating electrode potential, is also appreciably greater for negative corona.[2] Under these conditions, negatively charged carriers (molecular ions) leave the corona and wander towards the anode, their motion being determined by their mobility and the field in the transport zone. The concentration of these carriers varies from case to case, and from place to place, depending on the field; for the usual conditions found in practice, an average value is 10^8 cm.$^{-3}$. The dust particles present thus exist in an atmosphere of (uncharged) gas, admixed with a negative ion gas, the latter having an extremely small partial pressure (about 10^{-11} mm. Hg). From this standpoint, the charging of the dust particles can at once be understood. The ion gas naturally takes part in the general thermal motion, and its temperature is but slightly higher than that of the (uncharged) gas. The dust particles suffer collisions with ions about 10^{11} times less frequently than with neutral molecules, and they must gradually become more and more strongly charged negatively, because the ions give up their charge on reaching the surface of a dust particle, and because there is no mechanism available by which the dust particles can acquire a compensating positive charge. This charging takes place with a gradually diminishing velocity because of the corresponding increase in the force exerted on an approaching ion. The finite time of transit of a dust particle through the ion atmosphere sets a limit to the charge which may be acquired, which, as experiment shows,[3] is proportional to the radius, r, of the particles which are assumed to be spherical; for normal operating conditions the number of elementary charges, q, acquired by a dust particle, is given by $q = 2 . 10^6 . r$.

Apart from this purely kinetic treatment of the mechanism of charging, there is also the possibility that charging may occur in a region where there is a much higher field. In fact, such a field, under certain conditions, may be able to effect the further charging of a particle when the forces exerted by it on a colliding ion have become so large that, on account of its thermal motion alone, practically no further transfer of charge from ions is possible. The limiting charge, Q_g, which may be acquired by a particle under the influence of an external field, E, can be derived by considering the equilibrium between the forces at the surface of a particle, and the distortion of the (initially) homogeneous field by polarised dust particles, assumed spherical as before. If the dielectric constant of the particles is D, then Q_g in elementary units is given by

where e is the electronic charge.

For the conditions obtaining in practice ($E =$ about 3 kV. cm.$^{-1}$), and for particles greater than about 1μ diameter, it can then be seen from the above expression that the limiting value of the charge which may be acquired under the influence of the field may exceed that arising from gas kinetic effects alone, *i.e.* that above this particle size the limiting charge increases as the square of the particle radius. This relationship has been frequently verified by experiment, for example, recently by Fuchs, Petrjanoff and Rotzeig.[4]

The question now remains as to whether the time of transit of a particle under the conditions obtaining in practice is adequate to allow the limiting charge to be acquired. Pauthenier and Moreau-Hanot [5] have given the following expression for the growth of the charge with time :—

$$Q = Q_\sigma(\pi \,.\, b \,.\, n \,.\, e \,.\, t)/(1 + \pi \,.\, b \,.\, n \,.\, e \,.\, t),$$

where b is the mobility of the ions ($b = 600$ e.s.u.), n the carrier concentration (10^8 cm.$^{-3}$), and e the electronic charge. On inserting these values in the above expression, it is found that a transit time of 0·1 sec. is necessary for 90 per cent. of the limiting charge to be acquired. For a gas velocity of 2 m. sec.$^{-1}$, which is an average value for industrial practice, it is then seen that it would be necessary for the particle to traverse only 20 cm. in order to be charged ; this distance is negligible compared with the several meters of effective precipitator length usually employed.

(2) The Drift and Precipitation of Dust Particles.

Having derived the charge on the dust particles, it is now possible to discuss the velocity with which they drift to the anode, or precipitation electrode. Assuming, as before, spherical particles, the drift velocity, w, for particles of present interest (*i.e.* from 0·1 — 10μ diam.[6]) may be derived from Stokes' law, or

$$w = E \,.\, e \,.\, Q/(6\pi \,.\, \eta \,.\, r),$$

where η denotes the viscosity of the gas. The particles drift with this velocity w towards the anode where they remain and become precipitated. Although there is this loss of particles at the anode, the concentration of particles throughout the gas is maintained uniform by the turbulence of the streaming gas and also by the eddies due to the electric wind ; it can then be seen that the concentration must fall exponentially along the gas stream through the precipitator. This exponential relationship between the concentration and the time of transit, or the length of the precipitator, was demonstrated by Anderson and Horne in America at the time when the technical development of electrical gas purification was beginning. More recently, Deutsch [7] developed the complete expression relating the degree of purification ζ, defined as the ratio of the residual to initial dust content, to the drift velocity w, the mean gas velocity v, and the precipitator dimensions (length L, and electrode separation s). This expression takes the following forms :—

for wire-in-cylinder systems $\zeta = 1 - \exp. [- 2 \,.\, w \,.\, L/(s \,.\, v)]$,
for wire-and-plate systems $\zeta = 1 - \exp. [- w \,.\, L/(s \,.\, v)]$.

It is thus possible to calculate the dimensions of a precipitator for a specified ζ from given data for the dust laden gas. Alternatively, the correctness of the above expressions can be tested, for example, from

measurements of the variation of ζ with v, and from these w could be derived and then compared with the theoretically calculated value.[8]

The field strength in a precipitator, E, is mainly determined by the space charge associated with the drift of unipolar carriers, and a knowledge of E is necessary to calculate w and Q. For a wire-in-cylinder system Townsend has derived an expression from which it follows that E is simply determined by the current density and b, except in regions in the immediate neighbourhood of the wire; this expression is $E = (2i/b)^{0.5}$ where i is the current per cm. of precipitator length. For the conditions obtaining in practice i may be taken as 0·01 ma. (or 3·10^4 e.s.u.) cm.$^{-1}$ and, using as before, $b = 600$ e.s.u., it is then found that $E = 10$ e.s.u., or 3000 volt cm.$^{-1}$. The derivation of E for a wire-and-plate system is beset with considerable difficulties, and it is necessary to assume that, to a first approximation, the values of E will not differ appreciably from those in a wire-in-cylinder system. On introducing these calculated values of E into the expressions given previously for the charging and the mobility, it may be shown that small particles of diameter less than 1μ drift with a velocity of a few cms. sec.$^{-1}$ practically independent of their diameter, and that, on the other hand, larger particles drift with a velocity proportional to their diameter, for example, about 25 cm. sec.$^{-1}$ for a diameter of 10μ.

The very good agreement between calculation and experiment affords evidence that there is no process contributing appreciably to the removal of dust in electrical precipitators other than those already mentioned. In particular, contrary to earlier opinion,[9] the electric wind does not effect the directed transport of dust particles to the precipitation electrode, a conclusion that would be at variance with the continuity of the gas stream.[10]

(3) The Influence of Dust on the Electrical Conditions.

We will now turn to consider the effect of dust before and after precipitation on the electrical conditions in a precipitator; this is a matter of practical importance.

Uncharged dust has no effect on the corona discharge. The effect of charging the dust is to introduce a large number of carriers of greatly diminished mobility, and consequently a space charge. Whilst the fraction of the total current carried by the (charged) dust particles is little more than 1 per cent. under normal conditions, the space charge, being equivalent to the introduction of a negatively charged grid, has a considerable effect in diminishing the total current. It can be shown that the presence of this space charge necessitates a modification of the Townsend expression for the current-potential relationship in a wire-in-cylinder system, $i = V(V - V_c)$, in such a way that V_c is increased, the amount being numerically equal to the space charge per cm. length of the system;[11] an experimental verification of this deduction has been described by one of us.[12] In practice, the increase in V_c may amount to several kV., and leads to a diminution of the current, which latter effect may, however, be avoided by suitably increasing the electrode potential, V.

The effect on the discharge of the deposition on the anode of coherent layers of precipitated dust is much more complicated, and also introduces serious practical difficulties. The effect is mainly dependent on the structure and moisture content of the precipitated dust, and may,

therefore, take many forms. A systematic examination of the available technical data, together with laboratory experiments, has led at least to a qualitative elucidation of the principal phenomena.[13] A characteristic effect is the appearance of ionisation on the precipitated dust layer : this can lead either to a stabilisation of the discharge, or to a disruptive discharge, sparking. In the former case, there is an increase in the current and a decrease in the efficiency of precipitation ; in the latter case, the operating potential is diminished whenever spark-over due to the dust occurs, and consequently the efficiency of precipitation is also decreased.

The theoretical explanation of the foregoing effects arising from the precipitated dust layer on the anode may be expressed in the following terms. In the case of a layer of low ohmic conductivity, from dry dust, the potential across the layer due to the passage of the total current would amount to a considerable fraction of the electrode potential ; the current therefore tends to flow through cracks in the dust layer in which ionisation of the gas has occurred. If the dust layer is sufficiently homogeneous for the cracks, and hence the alternative current paths, to be uniformly distributed throughout the layer, the stabilising effect previously mentioned is attained. On the other hand, if the current flow through the layer is highly localised, then the resulting high current densities at these points give rise to conditions favouring the development of sparking.

Various devices are employed in practice in order to minimise these difficulties. The resistivity of the (precipitated) dust may be very greatly diminished by the introduction of moisture, either before or after precipitation. Further, by suitable choice of the geometry of the precipitation electrode, the formation of thick layers can be avoided, the dust being collected through slits or holes (" pocket electrodes," " high power electrodes "). The wave form of the electrode potential has also an influence of behaviour of a precipitator. Whilst a d.c. potential is naturally most effective for a speedy charging of the dust (its maximum value being set by the breakdown potential for the system), it has been found sometimes to be advantageous to super-impose a 50-cycle wave on the usual d.c. potential ; this is especially the case for dusts of low conductivity, and the effect is attributed to the possibility that this procedure affords for the " dust condenser " to discharge in the intervals of zero current, and thus avoid the building up of potentials which might otherwise lead to breakdown.

In conclusion, it may be remarked that the essential points of the theory of the physical processes involved in electrical precipitation are understood, and that further development will be concerned only with particular problems. Furthermore, the practical development of electrical precipitation has now been carried so far that serious difficulties may be anticipated in special cases only. The design of smaller and smaller units is, however, a field in which further development would be profitable. The production of these at an economic price, would be of importance to (national) hygiene, and the curve of development [14] given at the Second World Power Conference in 1930 would then show a sudden increase.

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[6] Green, *Trans. Faraday Soc.* *This vol.*, p. 1091.
[7] Deutsch, *Ann. Physik.*, 1922, **68**, 335.
[8] Mierdel, *Z. techn. Physik.*, 1932, **13**, 564 ; Mierdel and Seeliger, *Arch Elektrotech.*, 1935, **29**, 149.
[9] Ladenburg and Tietze, *Ann. Physik.*, 1930, **6**, 581.
[10] Deutsch, *Ann. Physik.*, 1931, **9**, 249 ; Mierdel and Seeliger, *loc. cit.*[8]
[11] Deutsch, *Ann. Physik.*, 1931, **10**, 847.
[12] Mierdel, *Wiss. Ver. d. Siemens-Konzerns*, 1934, **13** (2), 94.
[13] Mierdel and Seeliger, *loc. cit.*[8]
[14] Seeliger and co-workers, *2nd World Power Conference Report*, 1930, section 2., No. 145.

GENERAL DISCUSSION.[*]

Mr. A. G. Grant (*Darlington*) said : I would like to congratulate Meek and Lunt on their very interesting analysis of energy conditions inside the corona in a wire and tube discharge system.   It would be interesting to know if in their work they have been able to throw any light on or draw any conclusions in regard to the conception of " minimum corona energy distance " evolved by Peek in the States, and to some extent accepted here.   Peek's view is that in order that corona may occur, it is necessary that the gradient should exceed that necessary for breakdown for a certain minimum distance from the wire, this distance being vaguely connected with the minimum travel necessary for an ion to acquire ionising energy. It seems now that the very detailed analysis made by the authors ought to throw some light on this problem.

Dr. B. W. Bradford (*Billingham*) said : It is possible in practice to predict the performance of an electrostatic precipitator by the expression due to Deutsch.[1]   For the case of the wire in cylinder arrangement, this takes the form :

$$\frac{n_0 - n}{n_0} = 1 - e^{-\frac{2kvt}{R^2 \cdot \ln R/r}}.$$

Where n_0 and n are respectively the initial and final fume ion concentrations, k is the mean mobility of the fume ions, v is the applied voltage difference, t is the time of contact in the precipitator, R and r are respectively the radii of the outer and inner electrodes.

This formula is based on the simple assumptions :

(*a*) that the combined effects of turbulence and ionic currents preserve a uniform ionic concentration across the cross-section of the tube,

(*b*) that the field intensity can be expressed by the classical formula :—

$$X = \frac{1}{x} \cdot \frac{V}{\ln R/r}.$$

No assumptions are involved regarding variation of intensity of ionisation in the corona with field intensity, or the average number of ionic charges acquired by fume ions.

There is no doubt that the Deutsch formula is capable of giving an accurate expression of the efficiencies of electrostatic precipitators.   For example, by standardising conditions it can be used to determine the mobility of the fume ions in a homogeneous aerosol, and hence the particle

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[*] On the two preceding papers.
[1] *Ann. Physik*, 1922, **68**, 335 ; *Z. tech. Physik.*, 1925, **6**, 423.

size, using the expressions derived by Rohman [2] or Ladenburg,[3] for the relation between particle size and the number of charges on the fume ions. The method has been applied to H_2SO_4 mist, and has given excellent results.

It is suggested, therefore, that the factors discussed by the authors, while of fundamental importance in the theory of corona, are not limiting factors in electrostatic precipitators. It follows that no great increase in the efficiency of such precipitators can be expected by working under conditions of maximum energy efficiency of ionisation, whatever these may prove to be for the case of a corona discharge in a turbulent aerosol, which, as pointed out by the authors, are by no means identical with conditions in a particle-free gas.

Mr. A. G. Grant (*Darlington*) said : The Deutsch expression throws no light on the voltage-current characteristics of corona, and is to some extent an empirical value presupposing known corona conditions. Work of the type described by the authors is of fundamental importance as leading up to an exact knowledge of corona conditions and data for predicting them. In other words, it aims at elucidating corona discharge itself, rather than dust removal efficiencies in corona applications.

Dr. R. W. Lunt (*London*) said : (1) *In reply to Mr. Grant*, the authors have avoided any implications of Peek's " energy distance theory " by using experimental data for the corona diameter ;

(2) *In reply to Dr. Bradford* : The authors desire to say that they agree with the views of Mr. Grant ; the use of the term " efficiency of a precipitator " is a somewhat arbitrary and partial description of the performance of a precipitator if it is identified only with the fractional precipitation $(n_0 - n)/n_0$. The authors' paper refers to the energy efficiency of ionisation, and suggests by implication that this efficiency is one factor determining the energy efficiency of precipitation, η_D particles of dust or mist precipitated per unit of energy supplied. Clearly η_D is proportional to $(n_0 - n)/(I \cdot V)$ where I is the current through a precipitator maintained by an electrode potential V. The Deutsch expression for $(n_0 - n)$ is not in itself sufficient to predict the variation of η_D with V and r under otherwise constant conditions because it supplies no information on the corresponding variation of I with V and r.

It is, at least, a reasonable hypothesis that the rate of production of ions per unit of energy supplied will determine to some extent the rate of charging, and therefore also of precipitation, of aerosol particles per unit of energy supplied. It has been shown that there are reasons for believing that the energy efficiency for ion production may be increased above that for a standard precipitator by increasing V and diminishing r ; there is, therefore, reason to anticipate that such a variation of V and r will tend to increase η_D, and this is a result that cannot be inferred from a consideration of $(n_0 - n)/(I \cdot V)$ using the Deutsch expression for $(n_0 - n)$ alone.

[2] *Z. Physik*, 1923, **17**, 253.
[3] *Ann. Physik*, 1930, **4**, 863 ; *ibid.*, 1932, **14**, 510.

A COMMERCIAL PLANT FOR REMOVAL OF SMOKE AND OXIDES OF SULPHUR FROM FLUE GASES.

By G. Nonhebel.

Simultaneous removal of smoke, dust and acid constituents from flue gases by alkaline water in compact commercial plant has recently been achieved as a result of study of packings for absorptions towers. Such a plant is the Howden-I.C.I. grid packed gas washer, units of which were put into service at Swansea Power Station last year. Further units will shortly be in operation at the new Fulham Power Station. An account of this plant and process together with a survey of the problem of atmospheric pollution in large cities has already been given in Applied Science Journals.[1] The physical and chemical problems involved in the design of the plant are, however, of general interest.

Composition of Boiler Flue Gas.

For the specific case of boiler flue gas, the scrubbing plant may treat gas of composition :—

Grit and dust varying mostly from 5-100 microns	1-2 mgs./litre at N.T.P. for stoker firing. 5-15 mgs./litre for powdered fuel firing.
SO_2 . .	0·05-0·20 per cènt. (= 1·3-5·2 mgs. SO_2/litre).
SO_3 . .	Traces [2] up to 10 per cent. of the weight of SO_2.
HCl . .	Traces of the order of 0·1 mg. HCl/litre.
NO and NO_2	Traces of the order of 0·1 mg./litre of combined nitrogen.
H_2O . .	Partial pressure of 0·05-0·08 atm.
CO_2 . .	10-16 per cent. by volume.
O_2	9-3 per cent. by volume.

The temperature of the gas will lie between 110° C. and 150° C.

Description of Plant.

For a process for the removal of the stronger acids such as SO_2 from boiler flue gases to be generally applicable it is necessary to add alkali to the scrubbing water. The consumption of water by the process can then be minimised by recirculation of the wash liquor around the scrubbing towers. Lime or finely ground reactive chalk are the cheapest alkalies available and these are added in the form of a thin milk (5-10 per cent. solids).

Fig. 1 shows the principal items of equipment involved. The gas to be treated is brought by the flue 1 into a distribution chamber, which may be over 25 ft. long and of about 1 second's capacity and from which it flows laterally into scrubbing towers placed along the length of one or both its

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[1] Pearson, Nonhebel and Ulander, " The Removal of Smoke and Acid Constituents from Flue Gases by a Non-Effluent Water Process," *J. Inst. Fuel,* 1935, **8,** 119, and *J. Inst. Elec. Eng.,* 1935, **77,** 1.
[2] H. F. Johnstone, " Corrosion of Power Plant Equipment by Flue Gases," *Univ. of Illinois Engineering Expt. Station Bulletin,* No. 228, June, 1931.

sides.   These towers may be up to 12 ft. wide and are about 25-30 ft. high.   Uniform gas distribution up through the towers is achieved by primary elements 2, which consist of vertical wooden boards 3 ft. high and 3 ins. apart placed in echelon as shown in the diagram. These elements are fitted with $3\frac{1}{4}$-in. wide pear section tops which collect the whole of the water falling from the packing above and distribute it as a film upon both sides of the elements. The speed of the gas up the empty tower is about 5 ft./sec. The primary elements are supported, however, in such a way that the gap between the pear section tops is only about 1 in. so that there is an appreciable resistance to the flow of the gas which assists in the attainment of uniform distribution.

Most of the coarse dust, namely, about half of the total dust, and about half of the SO_2 in boiler flue gas, are removed by the water passing over the primary elements. This section of the plant can withstand dust loadings of even 30 mgs./litre such as may be
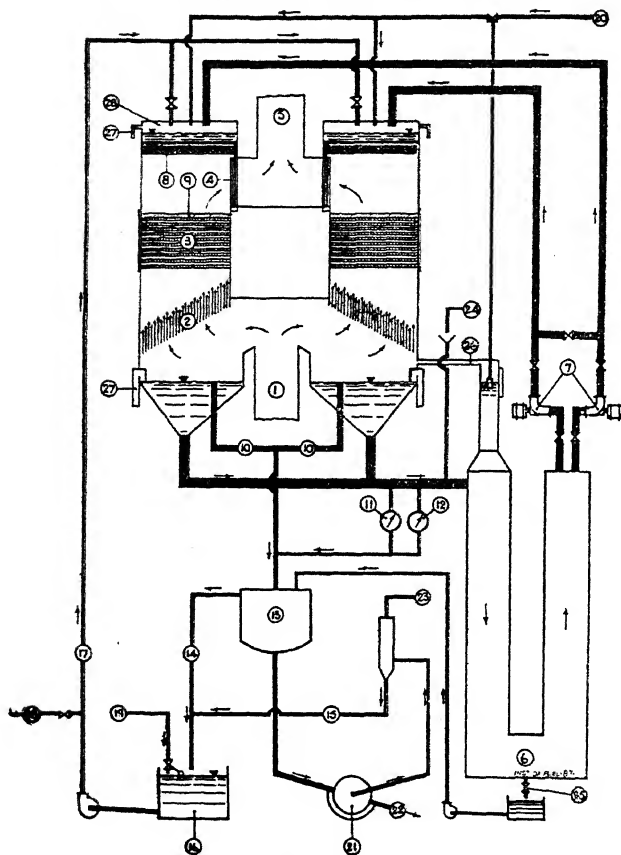
FIG. 1.

1. Gas inlet.
2. Primary elements.
3. Grid packing.
4. Spray eliminators.
5. Gas outlet.
6. Delay tank.
7. Recirculation pumps.
8. Liquor distributors.
9. Film feeders.
10. Purge.
11. p_H recorder.
12. Solids recorder.
13. Settler.
14. Clarified liquor from settler.
15. Clarified liquor from filter.
16. Mixed liquor tank.
17. Mixed liquor return.
18. To alkali preparation plant.
19. Make up water supply.
20. Emergency make up water supply.
21. Rotary vacuum filter.
22. Dewatered solids (rejected from system).
23. To vacuum pump.
24. Alkali supply and control.
25. Delay tank sludge cock.
26. Pressure equalising pipe.
27. Emergency overflows.
28. Liquor head tank.

Diagrammatic arrangement of Howden I.C.I. Flue Gas Scrubber system.

obtained from a cement kiln.   The final scrubbing is effected by a height

of only 3 ft. 6 ins. of a special open grid type of packing 3. The grids found most effective for this duty, as determined by high efficiency and low resistance, are composed of thin wooden laths 1 inch deep, 3/32 inch thick, held vertically ¾ inch apart by thin brass or wooden "carriers." The grids are piled on top of each other, the laths of one grid being at right angles to those immediately above and below. The grids are usually built for ease of handling in blocks four sections deep and 4-6 ft. square. The "carriers" are 12-15 ins. apart and are staggered so as to avoid division of the pile of grids into a number of small cells.

The gas rises through the grids and passes out through one or both of the long sides of the towers through spray eliminators 4. These consist of boards about 4 ft. high, 4 ins. wide, ¼ inch thick, and 1½-2 ins. apart arranged in a double V or zigzag formation. The height of these boards is chosen so that the velocity of the gas out of the tower does not exceed 6 ft./sec. From the spray eliminators the gas is led along flues to the boiler induced draught fan and delivered to the chimney.

Owing to the large volume of water required to wet the packing and to prevent scale formation thereon (see below), economy in washing water is achieved by recirculation of the used liquor around the scrubbing towers. The main liquor flow is shown by the heavy lines in the diagram. From the pumps 7 the liquor is fed to the head tanks 28, through pipes set at such an angle that the swirl produced is sufficient to prevent settlement of the dust, etc., in suspension. In the base of the head tanks are holes ¾ inch diameter, and about 9 ins. apart through which the water flows on to a 9-inch depth of liquor distributing grids 8. The latter consist of wood bars, ¾ inch square in cross-section and spaced ¾ inch apart, which serve to distribute the water from the nozzles as a fine rain on to the packing.

For efficient utilisation of the scrubbing fluid, it is important that it should flow as a film on the surface of the scrubbing packing. This is because the absorptive capacity of a simple spray is relatively low, since the relative turbulence between gas and liquid is low. The turbulence of the gas as it passes through the grid packing is, on the other hand, appreciable, and is sufficient to throw the humidified dust particles on to the liquor film, which then retains them. Moreover, the liquid is thoroughly mixed as it flows from each layer of laths to the layer at right angles below, and this mixing ensures that there shall be no appreciable concentration of dissolved SO_2 at the surface of the film which will reduce the absorption rate.

The rain of liquid is therefore fed as a film on to the grids by means of a number of laths 9, set at an angle like a horizontal venetian blind. These film feeders ensure that no free liquid falls through the ¾-inch square lattice of the grids.

The normal liquor recirculation rate which is required in order to give a sufficiently thick film on the grids to prevent ash deposition upon their surface is 7 litres/hour per cm. periphery of each grid or about 7000 litres/hour per square foot of cross-section of the grid. This gives a film thickness of 0·9 mm.

From the grids and primary elements, the liquid passes through a shallow hopper into a large capacity "delay" tank 6, from which it is pumped back to the scrubbing towers by the pumps 7.

Due to the use of a closed liquor system the water in circulation is saturated with respect to calcium sulphite and calcium sulphate, and can, under certain circumstances, become appreciably supersaturated. One of the principal problems involved in the design of the plant is the control of this supersaturation in order to prevent deposition of scale on the scrubbing surfaces which would choke the tower.

Supersaturated solutions of $CaSO_3$ and $CaSO_4$ are relatively stable even in contact with crystals of their solid phase, and about 3 minutes in each case are required for a reduction in supersaturation from 5 mg.

equivs./litre to 2 mg. equivs./litre above normal saturation in presence of over 3 per cent. by weight of their crystals. Fortunately supersaturated solutions of these salts do not begin to deposit crystals spontaneously on clean wood (free from crystals) until the level of supersaturation is somewhat over 5 mg. equivs./litre. Consequently the plant is designed so that the liquor is proportioned to the gas rate, its sulphur loading and the degree of oxidation occurring in order to keep the amount of $CaSO_3$ and $CaSO_4$ formed in each liquor recirculation below 3 mg. equivs./litre. The extent of oxidation which occurs when SO_2 is absorbed by this solution of calcium bicarbonate is only slightly affected by the oxygen content of the flue gas and is mainly dependent on the oxidation catalysts (Mn, etc.) derived from the lime and the ash and possibly by the small traces of oxides of nitrogen absorbed. With a plant on full load the proportion of total absorbed sulphur appearing as $CaSO_4$ varies from 30-50 per cent. with stoker fired boilers to 50-80 per cent. with powdered fuel boilers.

When the sulphur content of the flue gas is less than 3 mgs. SO_2/litre, the controlling factor in the size of the scrubbing towers is the maximum gas flow that can be passed through the grids without stripping off the liquor film.

From the last paragraph but one it follows that it is necessary to allow at least 3 per cent. of calcium sulphite and sulphate crystals to accumulate in the liquor and to allow time for crystallisation before pumping the liquor back to the scrubber if building up of supersaturation and consequent scale formation are to be avoided. In plants where the scrubbing towers are in an elevated position, the delay tank can conveniently take the form of a U tube supported on the ground as shown in the diagram. The diameter of the rising leg of the tube is chosen so as to prevent settlement of the suspended solids.

Accumulation of suspended solids above a predetermined level is prevented by purging a small flow of the liquor to a settler 13 or a rotary filter 21, where the solids are removed as a mud containing 30-50 per cent. of water. The clear liquor plus water required to make up losses in the mud and by evaporation is returned through the tank 16, and the pipe 17, to the head tank, where it reduces the supersaturation of the entering circulating liquor.

The quantity of purge is set by reference to an instrument 12, which indicates the specific gravity of the slurry. In one form of indicator this takes the form of a compressed air depth gauge used with a constant depth of flowing slurry.

Alkali Control.

The milk of lime or chalk for neutralisation of the absorbed SO_2 is added continuously at 24, just before the delay tank. The increase in p_H at this point reduces the solubility of $CaSO_3$ appreciably and assists rapid crystallisation of this compound.

For efficient SO_2 removal, and also in order to prevent corrosion of the steel towers and pipes it is necessary to control the p_H of the circulating liquor fairly closely at 6.3 ± 0.2 at the base of the scrubber. Addition of excess alkali is wasteful, as it is lost as $CaCO_3$ in the purge liquor. With control at p_H 6.3, the p_H after the delay tank seldom rises above 6.8, and since the liquor is saturated with CO_2, both lime and chalk are almost completely dissolved as $Ca(HCO_3)_2$, and this is the effective scrubbing agent. The alkali loss is not more than 10 per cent.

The p_H is measured by passing a small flow of hopper liquor to a cell 11, containing a glass electrode-calomel combination. The E.M.F. is measured on a Cambridge thermionic valve potentiometer worked off the power mains and the reading is recorded on a chart. Suitable relays can be fitted to the instrument to enable it to control the lime addition valve automatically.

It is found that
inactive after 5-10
5 per cent. HNO_3.

Moisture Content of Scrubbed Gases.—Since the grid scrubber is a highly efficient mass transfer apparatus the gas leaving the plant is saturated with water vapour and is cooled to the wet bulb temperature of the inlet gas. The circulating liquor is at the same temperature.

As the issuing gas is substantially free from SO_2 and SO_3, which might stabilise a mist cloud, the plume of steamy vapour which issues from the chimney rapidly dissipates and becomes invisible.

Draught
draught loss
water gauge.

Smoke from Cement Kilns.—The pilot plant has also been tested on gases from a cement kiln. In these experiments the amount of alkaline dust collected by the liquor from the gases was sufficient to neutralise all the SO_2. The calcium sulphite served also to absorb most of the H_2S in the gas.

Pilot Plant.—Fig. 2 is an isometric view of the complete Pilot Plant the Billingham works of Imperial Chemical Industries Limited, where the design details of the process were worked out. The various items of the plant can be clearly seen. The scrubbing tower was 4 ft. square.

Plant Efficiencies.—The table shows some of the efficiency figures that have been obtained with the Pilot Plant on full load, and also at the powdered fuel power station at Swansea.

Plant.	Substance Measured.	Concentration. Mgs./litre at N.T P.		Per Cent. Elimination.
		Inlet.	Exit.	
Pilot .	Dust from cement kiln	10·4	0·12	98·8
		31·9	0·35	98·9
	Dust from powdered fuel boiler	9·6	0·26	97·2
Swansea		11·8	0·21	98·2
		—	0·41	over 98
Pilot .	SO_2 and SO_3 measured as total sulphur	1·87	0·32	99·8
		1·76	0·0033	96·4
Swansea	SO_2 and SO_3 measured as total sulphur	0·642	0·0632	99·7
		0·834	0·0018	99·7
Pilot .	HCl	0·190	0·0020	96·4
	Oxides of nitrogen as nitrogen	0·171	0·0069	65
		0·246	0·060	63
			0·091	

The high efficiency of the plant for dust removal has also been amply shown by the ease with which it removed black smoke from a pulverised coal boiler when combustion conditions are deliberately made bad. The figures show, too, that the high efficiencies predicted from the Pilot plant experiments have been fully confirmed on full size commercial units.

of J.
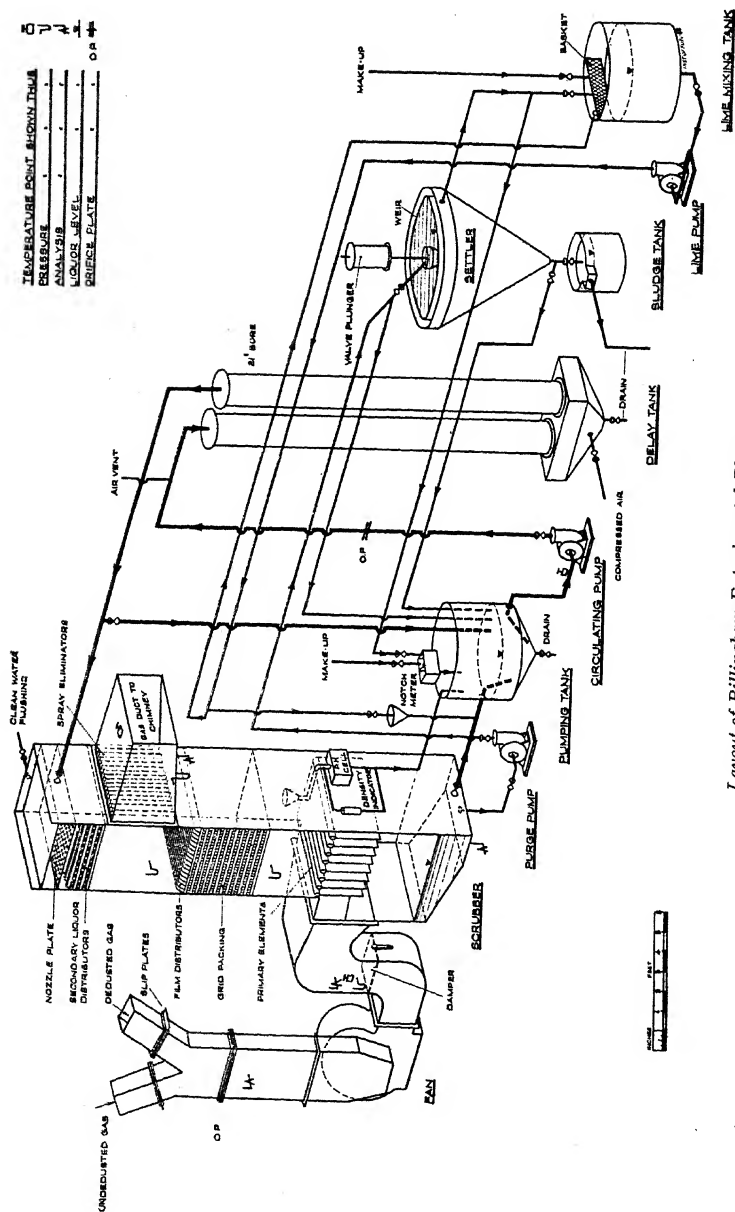
Layout of Billingham Experimental Plant.
FIG. 2.

GENERAL DISCUSSION.

Mr. W. A. Damon (*London*) said : As far as I am aware, there are only two plants where efficient removal of acidity from flue gases is practised. One is at Battersea Power Station, where the plant is remarkably efficient. Great credit is due to the London Power Co. for their efforts in this direction, but the Battersea scheme is not of very wide applicability in that it requires for its operation large volumes of naturally alkaline water, such as are available from the Thames. The Howden-I.C.I. plant described by Nonhebel is free from this disability, the only water required being that to make up loss by evaporation. In the event of ample alkaline water being available, can the scrubber operate without recirculation or is it necessary that the scrubbing liquor should have such an alkalinity that recirculation is necessary in the interests of economy ?

One would like to see a much wider application of flue gas washing. Dr. Pearson demonstrated in a paper before the Institute of Fuel [1] that the loss to the country occasioned by sulphur oxides in the atmosphere amounted to 10/- per ton of coal burned, and that it was, therefore, an economy to spend anything less than that sum on flue gas washing. The manufacturer, however, does not regard the matter quite in that light. Can Mr. Nonhebel tell us whether he can see any possibility of economy in the operation of the plant by making any use of the calcium sulphate mud which is produced.

Dr. R. Lessing (*London*) said that the successful elaboration of a plant and process for the complete purification of flue gases was one of the outstanding achievements in chemical engineering during the last few years. The work leading up to the design of plant and devising the process presented many problems in physical chemistry. Not the least was the prevention of incrustation from supersaturated solutions. He had pointed out six years ago the inexpediency of discharging the spent liquors into water courses and strongly advocated a cyclic, non-effluent system. He was also of opinion that the $CaSO_3$ primarily formed should be completely oxidised to $CaSO_4$. This could be done without difficulty and would eventually lead to the commercial utilisation of the product of reaction in form of $CaSO_4 . 2H_2O$.

Mr. G. Nonhebel (*Billingham*), in reply, said : It would be perfectly possible to use a straight through water system with the process provided sufficient water was available to irrigate the packing, and that water contained sufficient bicarbonate to neutralise the absorbed SO_2. Addition of lime to the inlet water in absence of the dissolved CO_2 present in the recirculating system gives a scale of $CaCO_3$ on the pipes and packing. Finely ground chalk is probably not sufficiently reactive. The separation of the dust from the used water of such a straight through system would undoubtedly cause difficulties, owing to the large volume of water involved.

One use to which the solids collected by the system could be put would be the manufacture of plaster. It would be necessary to incorporate in the liquor recirculating system an oxidiser of the type mentioned by Dr. Lessing in order to convert all the calcium sulphite to sulphate. With stoker firing the product would then contain 85-90 per cent. $CaSO_4 . 2H_2O$. Until large-scale plants are running, however, it is not possible to predict how the particle size will vary with the inevitable and frequent variations in load experienced in power stations, and reasonable uniformity is essential for such a product.

With very large plants there might be an economic case for utilisation of the mixture of ash and $CaSO_3$, etc., for the production of cement and sulphuric acid.

[1] *J. Inst. Fuel*, 1935, 119.

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AUTHOR INDEX.

The references in heavy type relate to the contributions which were the subject of general discussion.